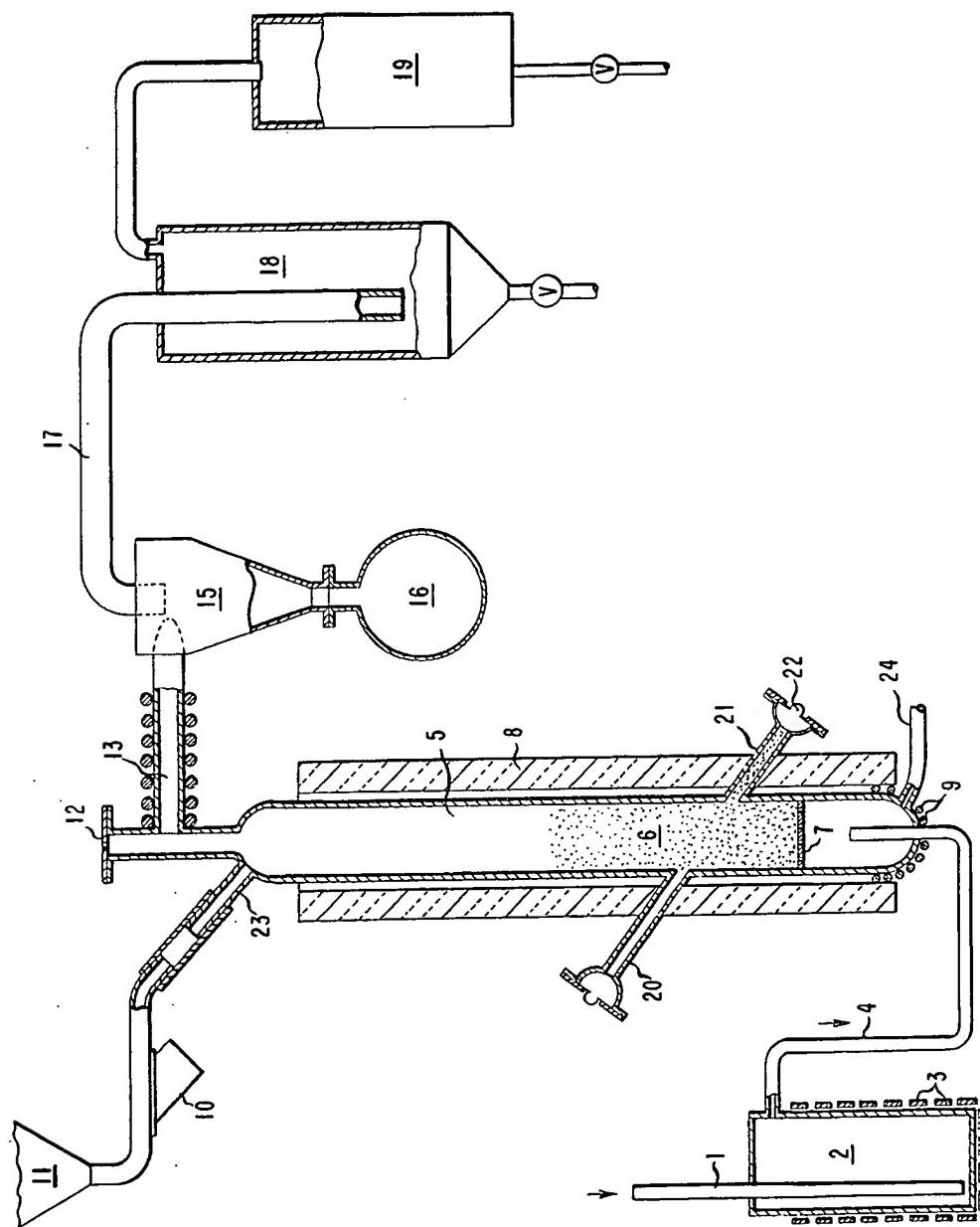


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PROCESS FOR ALUMINUM REDUCTION OF METAL HALIDES  
IN PREPARING ALLOYS AND COATINGS  
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PROCESS FOR ALUMINUM REDUCTION OF  
METAL HALIDES IN PREPARING ALLOYS  
AND COATINGS

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9 Claims. (Cl. 117—100)

This invention relates to the aluminum reduction of halides of metals from Groups IV, V, and VI of the Periodic Table.

Aluminum has been previously used as a reducing agent in the reduction of refractory metal halides. For example, titanium tetrachloride has been passed through a bed of aluminum at temperatures in the range of 400° C.—600° C. to form lower titanium chlorides. However, the reaction rate at these temperatures is relatively slow. On the other hand, at temperatures above 600° C., the aluminum particles soften and stick together, and yields become negligible.

The present invention concerns a process for operating an aluminum reduction of refractory metal halides in an agitated bed at temperatures above the melting point of aluminum. This process comprises contacting in a reaction zone the vapor of a refractory metal halide with an agitated bed of solid particles having aluminum at the surface thereof. The maintenance of aluminum at the surface of the bed particles may be accomplished by the use of a bed composed of aluminum alloyed with one or more of the Group IV, V, and VI refractory metals. Such alloys melt well above the melting point of aluminum (e.g., 96% Al-4% Ti melts at about 1000° C. and 98% Al-2% Zr melts at about 1000° C.), and it is found that they will react with the refractory metal halides at temperatures above aluminum's melting point without the formation of a liquid phase which would cause the particles to stick together. When such an alloy is used, the bed particle may be wholly of such alloy or the alloy may be present as a coating on an inert particle. As an alternative to these means for providing aluminum at the surface of the bed particles, it is possible to feed metallic aluminum particles to an agitated bed which may be composed of inert particles or metal particles composed of one or more of the Group IV, V, and VI refractory metals or alloys thereof with aluminum. When aluminum is introduced into the agitated bed, it is supplied at a rate relative to the introduction of the halide so that there is an insufficient amount of unreacted aluminum in the bed to form a liquid phase and cause the bed particles to stick together.

The reduction reaction of this invention is carried out at temperatures above the melting point of aluminum and the dew point of the metal halide vapor reactant, but below the melting points of the lower refractory metal chloride and alloys formed by the reduction reaction. Operating temperatures usually lie between 700°C.—1200° C., and preferably between 775° C.—1000° C. By contacting the metal halide with aluminum at the surface of the bed particles at these temperatures, there is a conversion of the refractory metal to a lower oxidation state which is accompanied by the formation of by-product aluminum halide which passes out of the bed as a vapor. Since the refractory metal products are produced in a solid state, they are easily recovered. Aluminum consumed during the reduction reaction may be replenished by the intermittent or continuous addition of aluminum particles to the agitated bed during the course of the reaction. Of course, such an addition should be slow enough to prevent

the accumulation of any appreciable amount of unreacted molten aluminum in the bed.

The refractory metal halides useful as starting materials in this invention are  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$ ,  $\text{ThCl}_4$ ,  $\text{VCl}_4$ ,  $\text{NbCl}_5$ ,  $\text{CrCl}_3$ ,  $\text{MoCl}_5$ ,  $\text{WCl}_6$ , and  $\text{WC}_5$ . Although silicon tetrachloride is not usually referred to as a refractory metal halide, it is felt that for the convenience of clarity in describing this invention, it is proper to include the halides of silicon within the term "refractory metal halides." In the process of this invention, the silicon halides are always reduced to elemental silicon. However, the other refractory metal halides may be either partially reduced to lower chlorides or completely reduced to the metallic state. In general, the formation of lower chlorides rather than complete reduction to the metal is favored by using lower temperatures, shorter contact times, or by restricting the amount of aluminum to near or below the stoichiometric requirement based on the amount of incoming chloride. However, by increasing the relative amount of aluminum, raising the temperature, and increasing the retention time, the reduction becomes more complete and the major product is the refractory metal alloyed with aluminum. It was also discovered that when the aluminum is fed to the top of the fluidized bed, there is a greater tendency toward lower chloride formation, while introducing the aluminum at the bottom of the bed favors reduction to the metal. This was surprising in view of the fact that a fluidized bed is considered to be a thoroughly mixed system. This effect may be due to the achievement of a relatively longer retention time in contact with aluminum-rich particles. The ratio of the amounts of vaporous chloride and aluminum supplied to the reaction zone is not at all critical provided the aluminum feed rate is below that which causes agglomeration of particles due to liquid phase. A large stoichiometric excess of aluminum operates to reduce the chloride more completely to an aluminum-rich alloy, the only limit being the formation of an aluminum alloy melting below the operating temperature. By changing the stoichiometry to a large excess of the vaporous chloride, the production of lower chloride is favored. Such large excesses of the chloride are used in obtaining partial reduction of the less active metals of the Fifth and Sixth Groups. Extremely large excesses, of course, result in non-reduction of part of the incoming chloride, but the process still operates to produce some lower chloride.

The attached drawing shows an apparatus which may be used to carry out the process of this invention.

Referring now to the drawing, the inlet pipe 1 serves to admit a stream of carrier gas such as argon to the vaporizer 2, which is kept at the desired temperature by heating element 3. The gas stream carrying the vaporous chloride passes through tube 4 to the base of the column 5. Tube 4 as well as the reaction zone is maintained above the dew point of the vaporous chloride being conveyed through it. The body of solid particles to be fluidized is supported in the column by the perforated plate 7. The column itself which forms the reaction vessel may be constructed of fused silica. The cooler accessories such as pipes 4, the aluminum feeder 10, hopper 11, and the various collectors and traps 15, 18, and 19 may be made of glass or a suitable metal and connected to the silica with suitable ground joints or couplings. The base of the column is heated by elements 9 and the insulating jacket 8 may contain heaters to maintain the desired temperature in the particle bed or reaction zone 6. The top of the column and exit arm 13 are also heated at least above the condensation temperature of  $\text{AlCl}_3$ . The entering tube 23 admits aluminum, preferably in granular form, from the vibrating feeder 10 through a flexible connector. The top opening 12 may be used for the initial charging of the fluidizable solids as well as

for insertion of a thermocouple. Once the relationship between the inside temperature at 6 and the outer wall temperature is established experimentally, the internal thermocouple is preferably removed and the temperature control derived from thermocouples placed between the column 5 and the insulation 8. The cyclone 15 and collector 16 are maintained above the dew point of the aluminum halide by-product. Condensers 18 and 19 are used to collect unreacted refractory metal halide and by-product aluminum chloride. When the refractory metal halide is titanium tetrachloride or silicon tetrachloride, condenser 18 is cooled to condense the aluminum halide but maintained above the dew point of the refractory metal halide which is subsequently recovered in condenser 19. With the other refractory metals, condenser 18 is cooled to condense the refractory metal halide but maintained above the dew point of aluminum chloride which is subsequently recovered in condenser 19. The side arm 20 is an alternative location for feeding aluminum. The tube 24 supplies auxiliary fluidizing gas to the bed. Side arm 21 with the plug 22 serves as a discharge means for the solid particles in 6. The system is of course protected from contaminating entrance of air, moisture, etc.

A preferred embodiment of this invention comprises feeding titanium tetrachloride up through a fluidized bed of inert particles, such as sand, maintained between about 775° C. and 1000° C., while feeding aluminum particles to the top of the fluidized bed at the rate of about two atoms of aluminum for three molecules of  $TiCl_4$  fed, and passing the products of the reaction evolved from the top of the bed into a second zone where they are cooled below 700° C.; preferably, they are rapidly cooled to temperatures in the range of about 300° C. to about 600° C., whereupon a product rich in titanium dichloride is recovered.

The second or quenching step, when applied to this process, results in a lower chloride product of minimum valence, such as a product rich in  $TiCl_2$ ,  $ZrCl_2$ , or  $HfCl_2$ . The cooling may be provided in a number of ways. A cooled walled passage suffices although the product tends to build up on the wall and a scraping mechanism is employed for its recovery. Quenching by the introduction of cooler inert gases or vapors is useful. Recycling of aluminum chloride, especially in the condensed state, effects excellent cooling. The quench cooling may be applied at the cyclone collector shown in the drawing for separating the lower chloride product from by-products and carrier gases.

In another preferred embodiment, niobium pentachloride is vaporized and carried in a stream of argon into a fluidized bed of niobium-aluminum alloy particles maintained at about 775–1000° C. Granular aluminum is simultaneously fed to the bed to replenish the aluminum consumed in the by-product aluminum chloride and in the alloy formed in the process. The particulate niobium-aluminum alloy product is periodically or continuously removed from the fluidized reaction zone and recovered.

For a clearer understanding of the invention, the following specific examples are given. These examples are intended to be merely illustrative of the invention and not in limitation thereof. Unless otherwise specified, all parts are by weight.

#### Example I

An apparatus as illustrated in the drawing was used for the reduction of  $TiCl_4$ . The reaction column 6 was 3.5" I.D. and contained four pounds of -90+120 mesh alumina particles. These particles were maintained at 875° C. and fluidized by a flow of argon at .374 linear ft. per second, the gas velocity calculation being based on the cross-sectional area of the empty column. In this example, the vaporizer 2 was maintained at 200° C. and the  $TiCl_4$  was metered into the vaporizer where it flash-vaporized into the argon stream. Pure granular alumi-

mum metal, +140 –10 mesh, was fed to the top of the column. 85 grams of aluminum and 2 lbs. of  $TiCl_4$  were fed simultaneously over a 15 min. period. The pipe 13 connecting the column with the cyclone was held at about 400° C. and the cyclone separator held at about 300° C. The aluminum chloride condenser 18 was held at 150° C. while the condenser 19 was water cooled to recover the unreacted  $TiCl_4$ . During this period, 403 grams of fine, crystalline lower chloride of titanium,  $TiCl_{2.2}$ , were collected in the cyclone, representing a yield of 67% of the  $TiCl_4$ . About 250 gms. of  $TiCl_4$  were recovered at the condenser. About 12 gms. of titanium alloyed with aluminum was found in an Al-Ti coating on the alumina bed particles. In a subsequent operation of similar nature, it was found that the titanium alloy residue in the bed could be converted to lower titanium chloride and aluminum chloride by merely discontinuing the aluminum feed for a few minutes while continuing the flow of  $TiCl_4$  which reacts with the titanium as well as the aluminum in the alloy coating.

#### Example II

The apparatus used was essentially the same as used in Example I, except that the silica reaction column was about 6' long. The column was filled to a depth of about 1 ft. with 100 mesh alloy of the approximate composition: AlTi. Argon was admitted to fluidize the alloy particles and the temperature of the bed raised to 950° C. The vaporizer was heated to 250° C. and  $TiCl_4$  admitted at 2 gram mol per minute. Aluminum powder was simultaneously fed to the lower portion of the bed through inlet 20 at a rate corresponding to about 3.5 gram atoms per gram mol of  $TiCl_4$ . These conditions involve a longer retention time in the bed, a higher temperature and greater proportional aluminum feed than in Example I, and such conditions favor the production of a titanium-aluminum alloy which builds up on the initial alloy particles. After 20 minutes of operation, approximately 20% of the Ti values fed to the reactor was collected as lower chlorides in the cyclone separator, while 50% was converted to metallic Ti-Al alloy and the remainder was recovered in the condenser as unreacted  $TiCl_4$ . The individual alloy particles recovered from the bed varied somewhat in composition. The particles were well mixed to insure uniformity, and a sample was then analyzed and found to contain about 30% Al.

#### Example III

$TiCl_4$  was reduced as in Example I except that when the  $TiCl_4$  was fed to the vaporizer the argon supply was cut back to zero during the first 3 min. of the run, thus depending on the flow of  $TiCl_4$  and by-product  $AlCl_3$  vapors to maintain the fluidized condition in the bed. The products obtained were approximately the same as in Example I.

#### Example IV

In an apparatus as shown in the drawing, the vaporizer was provided with a series of shelves around the inside walls. These shelves were charged with solid zirconium tetrachloride. The incoming argon and the vaporizer were held at 300–310° C. to provide approximately an equi-volume mixture of argon and  $ZrCl_4$  vapor which fluidized a bed composed of -100 +200 mesh Zr maintained at 850–900° C. Aluminum particles were fed to the top of the bed at a rate stoichiometric with the formation of  $ZrCl_2$ . This rate was adjusted on the basis of the rate of argon flow since both the argon and the  $ZrCl_4$  were fed at the same volume rate. After about one-half hour of operation, zirconium values in the form of a zirconium-aluminum alloy, zirconium dichloride, and zirconium tetrachloride were found, respectively, in the bed, the cyclone separator, and the first condenser.

## Example V

To illustrate the effect of temperature control on this process, an apparatus as shown in the drawing was used. The reaction chamber was a silica tube six feet high with a three-inch inside diameter tube for the reaction chamber. Sand was used as the inert bed material, while the argon and  $TiCl_4$  mixture was fed at a rate which gave a retention time of 4.5 seconds in the bed. Aluminum was simultaneously fed to the top of the bed at the rate of 2 mols Al for each mol of  $TiCl_4$ . The resulting titanium lower chlorides were carried out with the vapors and recovered in a cyclone separator.

In the first run, the reaction temperature was  $775^\circ C$ , and in the second run, the reaction temperature was  $900^\circ C$ . In both the first and second runs, the cyclone separator was operated at  $500^\circ C$ . A third run was made at  $900^\circ C$ , but in this run the silica tube leading to the cyclone separator and the separator itself were cooled to about  $350^\circ C$ . The results were as follows:

Run	Reaction Temp.	Ti Yield in Lower Chloride, Percent	Valence of L.C.
1.....	775	37	2.4
2.....	900	52	2.28
3.....	900	54	2.23

The alloy initially produced in this invention by the simultaneous introduction of aluminum and the refractory chloride to the reaction zone may be quite high in aluminum. However, according to this invention, it is possible to reduce the aluminum content of the alloy by stopping the aluminum feed while the flow of vaporous chloride is maintained. The high-aluminum alloy particles will then react with the chloride. The aluminum of the alloy seems to react faster than the refractory metal, and the result is an alloy of lessened aluminum content; e.g., as low as 3 to 6% Al in the case of titanium and somewhat lower in the case of the less reactive metals.

Other embodiments not described above may also be employed in this invention. The vaporous chloride supplied to the reaction zone may be produced by any suitable means. Although vaporization prior to introduction into the fluidized solids is preferred, vaporization in the fluidized zone is something practicable. For example, the less volatile normally solid chlorides, some of which sublime, such as  $ZrCl_4$ , may be fed as powder or crystals to the reaction zone where vaporization occurs promptly at operating temperatures. If meltable chlorides are fed in solid form, the rate of feeding should be such that vaporization is complete before any appreciable quantity of a liquid phase develops in the bed. The aluminum particles fed to the bed should be relatively small so as to provide as much reaction surface as possible, but they should be above the size which will become entrained in the gas stream and carried out of the reactor with the products and by-products. The correct sizes may be determined experimentally for the operating gas flows which are being used. Since the instant process is carried out at temperatures of about  $700^\circ C$  or higher, it is obvious that a particle of pure aluminum, which melts at about  $660^\circ C$ , could not long exist in the solid state in the reaction zone. The pure aluminum reducing agent can, however, be fed at substantially the rate at which it is consumed without forming a distinct liquid phase in the reaction zone. It is probable that the aluminum reacts as soon as it reaches melting temperature to form a non-liquid alloy. Any traces of liquid aluminum are spread by the vigorous action of the bed over the particles in a film so thin and short-lived that no evidence of a liquid phase appears. Theoretically, there is an upper limit on the rate at which aluminum may be fed to the reactor, depending upon the rate at which the other reactants are fed. However, the

reaction has proved to be so rapid that no maximum rate has yet been found experimentally. It is also possible to feed molten aluminum to the reaction zone provided the feed rate is controlled so that the aluminum is consumed rather than being allowed to form a pool of unreacted aluminum. The aluminum may, of course, be supplied as particles of an appropriate aluminum-rich alloy. For example, Al-Si may be fed to the reactor to reduce  $SiCl_4$  or to reduce other elements, such as  $TiCl_4$ . Al-Ti is another such alloy. Alloy produced in the reaction may be removed intermittently or continuously during the reaction to regulate the bed volume or to maintain the correct particle size for fluidization. The larger particles may be selectively removed from the bottom part of the fluidized bed. The bed material may also be removed in part, sized and returned. Such a step helps to remove fine particles which have resulted from erosion or from chemical action on the initial alloy particles. If fine particles are not removed or enlarged by setting up alloy-producing conditions in the reaction zone, these fines may carry over undesirably to the lower chloride collection zone.

In the process of this invention, the main reaction is thought to take place at the solid surface containing the aluminum. However, some associated reactions may occur near by in the vapor phase. To facilitate the reaction, there should be good contact between the incoming gaseous reactants and the reaction surface. The best way of achieving this desired contact is in an agitated bed of particles containing available metallic aluminum. Agitation is best obtained by fluidization of the particles by the reactant gases and their carrier gases. Another alternative, usually less desirable, is to feed the higher chlorides to a rotating or tumbling reaction chamber or to a zone wherein the particles are agitated.

Carrier gases may be used to help fluidize the particles and to convey the vaporous chlorides into the reaction zone. These gases may be chosen from the inert gases like argon, helium, neon, etc., or recycled aluminum chloride vapor. Hydrogen may also be used, although due to its inflammability, a hazard is introduced. The hydrogen is not consumed as a reducing agent in the presence of aluminum, and hence is substantially inert. These gases and vapors which constitute the process fluids of this invention also carry the solid lower chloride product particles out of the reaction zone for subsequent separation and recovery.

The temperatures maintained in the process steps following the reaction zone are governed by the properties of the substances produced. The temperatures are usually successively dropped on going from the reaction column through the lower chloride product collection, the higher chloride recovery, and the aluminum chloride condensation. When titanium tetrachloride is the reactant, the aluminum chloride is condensed before the residual  $TiCl_4$ . In the lower chloride collector, which may be a cyclone type or a high temperature filter, the temperature is kept above the dew point of both the aluminum chloride and the unreacted higher chloride, and preferably above the boiling point of  $AlCl_3$ , to prevent adsorption of the aluminum chloride on the lower chloride product.

Elements other than the refractory metals having vaporizable chlorides reducible by aluminum may be co-reduced in this process to form part of the alloy end product. Examples of such chlorides are  $BeCl_2$ ,  $BCl_3$ ,  $FeCl_3$ ,  $PdCl_4$ ,  $PtCl_4$ , and  $SnCl_4$ . Frequently, mere traces of these elements will greatly benefit an alloy.

The inert particles used in this invention are comprised of substances which have melting and thermal decomposition points above the operating temperature. They should be mechanically strong enough to resist any substantial pulverizing by the agitation employed, at least until protected by the alloy coating. They should be capable of holding the alloy coating and substantially non-reactive with the alloys or other ambient substances. Suitable inert materials are sand, silica, alumina, quartz,

zirconia, zircon, magnesium oxide, calcium oxide, porcelain, silicate minerals, fluorspar, sodium fluoride crystals, etc. They should be of proper size to be satisfactorily agitated or fluidized in the reaction zone without being entrained in the gas stream to the extent that they leave the reaction zone. This may, of course, be controlled by known factors including shape and size of cross-section of the reactor, etc. in relation to the quantity of gases used.

In the foregoing discussion, it has been shown that both refractory metal particles and inert particles become coated with various aluminum alloys while in the reaction zone. This invention, therefore, includes the process of producing such alloy-coated particles. For example, the particles used in the bed may be spheres, rods, fibers, flakes, etc. designed for a subsequent use such as grinding media or specialty pigments or fillers. This coating step is not limited to the principal bed particles which may be powders or coarse particles capable of being agitated or fluidized, but may be applied to larger bodies suspended in the fluidized bed. One particularly useful application is coating turbine blades with an oxidation-resistant alloy containing, for example, aluminum, tantalum and silicon. Various metal working tools and extrusion dies may be coated with wear-resistant alloys by suspending them in a suitable bed where the aluminum reduction of the chlorides of the alloy-forming metals is being carried out. In many cases, the alloy coating will be initially too high in aluminum. As previously explained, this aluminum may be decreased to a desired level by an after-treatment with the chloride of one or more of the refractory constituents of the alloy. For example, a steel die may be coated with an alloy containing Al, Mo, and Si by suspending it in a fluidized bed of sand while feeding aluminum,  $\text{MoCl}_5$ , and  $\text{SiCl}_4$  to the bed. When a suitable layer of the alloy is formed, the aluminum feed is stopped, and the flow of  $\text{MoCl}_5$  and/or the  $\text{SiCl}_4$  is continued to deplete the aluminum content of the alloy. Many variations are possible in this application of the invention with respect to both the composition of the coating and the order in which the refractory elements are deposited on the object. Thus, multiple layers of varying or graded composition may be formed. Such deposits may, of course, be subject to subsequent heat treatments for the purpose of homogenizing or diffusing into the base metal. Ceramic or high-melting glass bodies may be similarly coated. Sheets or other forms may be hung in the fluidized solids reaction zone to be given a conductive or reflecting coating.

The process of this invention has various uses since two general types of product result: namely, alloys and lower chlorides. In either case, the process shows clear advantage over prior art methods. For example, refractory metal alloys useful as master alloys are produced directly in powder form, thus eliminating the work of melting, casting, and grinding to powder. As already described in Example I, these alloys are formed as thin coatings on the particles in the reaction zone. This offers the unique possibility of placing objects to be coated directly in this zone.

The lower chlorides produced by this method are exceptionally free of contamination. A small trace of  $\text{AlCl}_3$  may be adsorbed thereon, but heating in a vacuum or stream of inert gas will reduce this to substantially zero. These pure lower chlorides are highly suited for addition to electrolytic processes wherein they are reduced to the metal.

There are several commercial uses for the lower chlorides such as  $\text{TiCl}_3$ ,  $\text{ZrCl}_2$ ,  $\text{TiCl}_2$ ,  $\text{CrCl}_2$ , in their substantially pure form. When they are produced by known methods using sodium or magnesium as reducing agents, the lower chloride products dissolve in the by-product  $\text{NaCl}$  or  $\text{MgCl}_2$  and the pure product cannot be isolated. In the case of the prior art reduction by aluminum at temperatures up to  $600^\circ \text{C}$ , it is difficult or impossible

to completely consume the aluminum. This aluminum residue is also very difficult to separate from the lower chloride product, and its presence impairs its utility. In the preparation of the lower chlorides according to this invention, the lower chloride product is separated from the aluminum as a result of being swept out of the reaction chamber, whereupon it is collected as a crystalline powder. Advantageously, the method is ideally adapted to continuous operation for production of both lower chlorides and the alloy particles. The further advantage of this invention lies in the unique method of coating particles and solid objects with the refractory alloy composition produced.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the chemical reduction with aluminum of a refractory metal chloride selected from the group consisting of  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$ ,  $\text{VCl}_4$ ,  $\text{NbCl}_5$ ,  $\text{CrCl}_3$ ,  $\text{MoCl}_5$ ,  $\text{WCl}_6$ , and  $\text{WCl}_5$ , which comprises contacting in a reaction zone substantially free of any liquid phase the vapor of at least one of said chlorides with an agitated bed of solid particles, said particles having aluminum at the surface thereof, said reaction zone being maintained at a temperature above the melting point of aluminum and the dew point of the chloride vapor and below the melting point of the refractory metal products being produced, thereby forming by-product aluminum trichloride vapor and solid products containing said refractory metals in a lower state of oxidation.

2. The process of claim 1 in which the refractory metal chloride is titanium tetrachloride.

3. The process of claim 1 in which the refractory metal chloride is niobium pentachloride.

4. A process for preparing alloys which comprises feeding aluminum and at least one vaporous, refractory-metal chloride selected from the group consisting of  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$ ,  $\text{ThCl}_4$ ,  $\text{VCl}_4$ ,  $\text{NbCl}_5$ ,  $\text{CrCl}_3$ ,  $\text{MoCl}_5$ ,  $\text{WCl}_6$ , and  $\text{WCl}_5$ , to a reaction zone containing a fluidized bed of particles of a refractory metal of a said chloride maintained in the temperature range of  $800^\circ \text{C}$ . to  $1000^\circ \text{C}$ ., said aluminum being fed at a rate less than that which causes agglomeration of said particles and in at least the stoichiometric proportion to completely reduce said vaporous chloride, removing aluminum chloride by-product vapor from said bed and recovering additional refractory metal alloy formed in said bed.

5. The process of claim 4 wherein the aluminum is fed to the lower portion of the fluidized bed.

6. A process for coating a solid object with metal comprising contacting in a reaction zone substantially free of any liquid phase a vaporous, refractory metal chloride selected from the group consisting of  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$ ,  $\text{ThCl}_4$ ,  $\text{VCl}_4$ ,  $\text{NbCl}_5$ ,  $\text{CrCl}_3$ ,  $\text{MoCl}_5$ ,  $\text{WCl}_6$ , and  $\text{WCl}_5$ , with an agitated bed of solid particles, said particles having aluminum at the surface thereof, said reaction zone having suspended therein and in contact with said solid particles the solid object to be coated, maintaining said reaction zone at a temperature above the melting point of aluminum and the dew point of the chloride vapor and below the melting point of the refractory metal present in said chloride, thereby reducing said vaporous metal chloride with said aluminum and forming a metal coating on said solid object.

7. The process of claim 6 wherein the metal chloride is titanium tetrachloride.

8. The process of claim 6 wherein the metal chloride is niobium pentachloride.

9. The process of claim 1 wherein there is additionally present a minor amount of vaporous chloride of an

element selected from the group consisting of beryllium, boron, iron, palladium, platinum, and tin.

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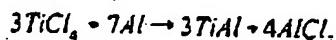
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## Titanium Aluminide Powder Production Via Reaction Between $TiCl_4$ and Al

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### Abstract

The feasibility of producing TiAl and other titanium-aluminide compounds by reacting Al with  $TiCl_4$  has been explored. This process is similar to the well known Kroll and Hunter processes for producing pure Ti. The chemical reaction for the formation of TiAl from  $TiCl_4$  and Al is as follows:



Based on available thermodynamic data, calculations revealed this reaction is energetically favored above 600°C. At lower temperatures  $TiCl_4$  is only partially reduced to  $TiCl_3$  and  $Al_2Ti$ . Experiments, utilizing a fluidized bed reactor, were used to react Al powder with  $TiCl_4$  at either 600 and 740°C, and the resultant powder was characterized by X-ray diffraction. At 600°C the powders transformed to  $Al_2Ti$  and  $Al_3Ti_2$ . At 740°C, the product was dependent on the size of the initial Al powder in the bed. Small Al powders (<100  $\mu m$ ) transformed to a combination of  $Ti_3Al$  and TiAl, whereas, larger powders transformed to  $Al_2Ti$  and TiAl. The results demonstrate that it is possible to produce aluminides by reducing  $TiCl_4$  with Al; however, to produce a uniform

reaction product, such as single phase TiAl, precise control over the reaction conditions is required.

### Introduction

Titanium-aluminide based alloys are emerging as a potential structural material. These alloys possess numerous desirable properties [1], such as a low density ( $3.8 \text{ g/cm}^3$ ), high melting point ( $1460^\circ\text{C}$ ), high modulus (160–180 GPa), high strength ( $\sigma_y = 350$ – $600 \text{ MPa}$ ) and useful oxidation resistance (up to  $800^\circ\text{C}$ ). Further, recent advances in alloy development have solved the problem of low temperature brittleness of the compound. For instance, TiAl alloys have measured room temperature fracture toughness as high as  $35 \text{ MPa}\cdot\text{m}^{1/2}$ , and room temperature tensile ductility of 4 percent [1]. However, presently the cost of manufacturing components from TiAl has hindered wide spread use of this alloy, particularly for non-aerospace/defense applications [2]. Thus, there is a need for low cost processing of TiAl based materials. Most cost reduction efforts have focused on secondary operations, such as casting and forming. However, regardless of whether the final component is fabricated via powder or melt processing, the source for the starting TiAl stock always is elemental Ti and Al. While a large percentage of cost can be attributed to secondary operations, the cost of primary operations (e.g.,

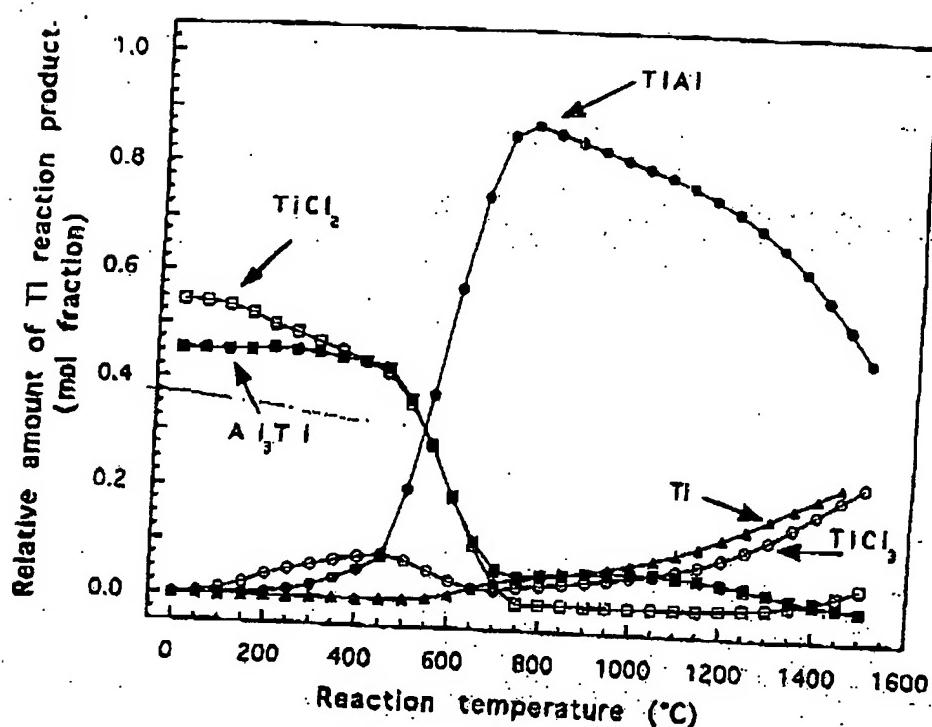


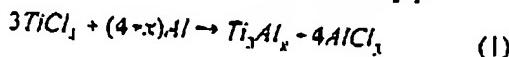
Figure 1. An equilibrium diagram for the Ti-containing reaction products for reaction (2).

those associated with the raw materials) is ignored in many cost reduction schemes. This is due, with few exceptions [3,4], to a dearth of information and research concerning primary processing of advanced materials like TiAl. The present research is concerned with modifying the Ti reduction process to form TiAl directly from the aluminothermic reduction of titanium-tetrachloride ( $TiCl_4$ ).

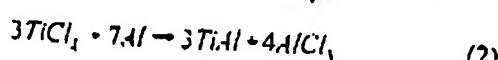
#### Thermodynamic Analysis of Aluminothermic Reduction

Conventionally, Ti is produced by, first, chlorinating  $TiO_2$  to form  $TiCl_4$ ; and then reducing the  $TiCl_4$  with either Mg (Kroll Process) or Na (Hunter Process) to form Ti and  $MgCl_2$  or  $NaCl$ , respectively. The salt is separated (leached) from the Ti (typically in sponge form), which is subsequently melted to form a Ti-ingot and remelted to form a Ti-alloy.

It may be possible to form titanium-aluminide compounds directly by reducing  $TiCl_4$  with Al, as follows [4]:



The corresponding chemical reaction for producing TiAl ( $x=3$ ) is as follows:



It is possible that this reaction may not be thermodynamically favored under certain conditions. That is, Al may only partially reduce  $TiCl_4$  to form any myriad of potential reaction product combinations, such as titanium-chlorides ( $TiCl_3$  or  $TiCl_2$ ), aluminum-chloride ( $AlCl_3$ ), and titanium-aluminides ( $TiAl_3$ ,  $Ti_2Al_5$ ,  $Ti_3Al$ ), and residual elemental Ti and Al.

Equilibrium calculations were carried out for the Ti-Al-Cl system using HSC® chemical reaction and equilibrium software and thermochemical data base [5]. Figure 1 is an HSC generated equilibrium diagram for reaction (2) as a function of temperature. For simplicity, only the concentrations of the relevant Ti-containing reaction products (i.e., titanium-chlorides and titanium-aluminides) are plotted. The available thermodynamic data predicts that at low temperatures (e.g., less than 600°C) Al will only partially reduce  $TiCl_4$  to  $TiCl_2$  and  $Al_3Ti$ . At operating temperatures above about 600°C, reaction (2) is thermodynamically favored. In fact, near complete conversion of  $TiCl_4$  to TiAl is predicted at about 700°C (i.e., the mole fraction of TiAl approaches 1.0). It also is interesting to note, that at extremely high operating

\* Reference to specific products does not imply endorsement by the U.S. Department of Energy.

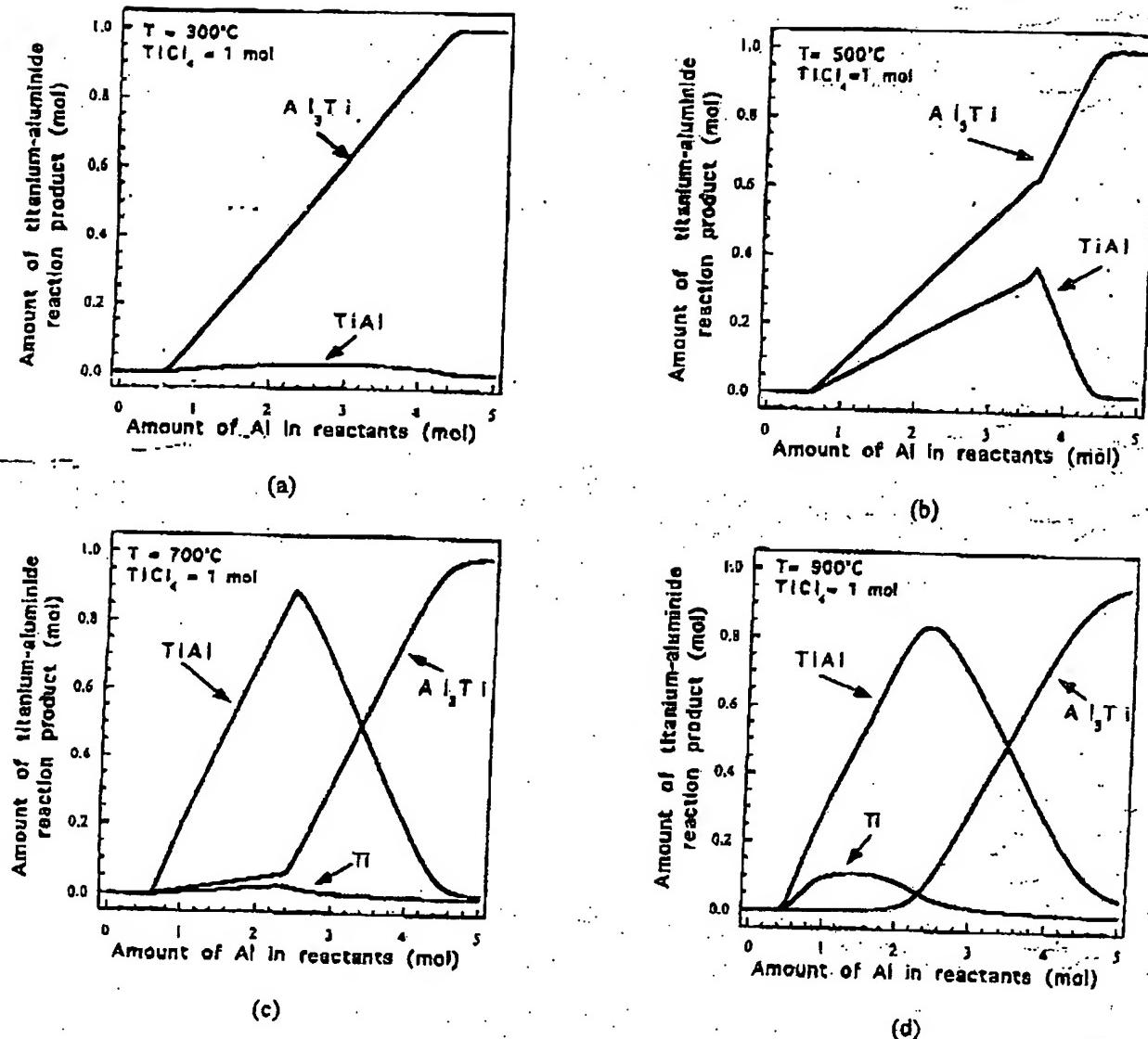


Figure 2. Influence of Al content on titanium-aluminide reaction products at: (a) 300; (b) 500; (c) 700; and (d) 900°C.  $TiCl_4 = 1$  mol.

temperatures (e.g.,  $> 1000^\circ C$ ). pure Ti is a thermodynamically predicted reaction product.

Figure 1 was generated for a stoichiometric concentration of reactants (i.e., 3 moles  $TiCl_4$  and 7 moles Al). Of course, it is feasible to operate with different amounts of reactants in non-stoichiometric conditions. Figure 2 shows the effect of Al content on the equilibrium aluminide reaction products at 300, 500, 700 and 900°C. These calculations were generated with a constant  $TiCl_4$  content of 1 mol. Therefore, an Al content of 2.33 mol corresponds to the stoichiometric amount required for reaction (2). At the lower temperatures the reaction product is independent of the concentration of the reactants (Figs 2a). That is,  $Al_3Ti$

is the favored reaction product (Fig 2a). However, at elevated temperatures, the reaction products are very much dependent on the relative concentration of the reactants (Figs 2b, 2c and 2d).  $TiAl$  is the predominate (or favored) reaction product when the ratio of Al to  $TiCl_4$  reactants is less than about 3.5. As the ratio of Al to  $TiCl_4$  increases, the excess Al will further react with any aluminides that have formed from the  $TiCl_4$  (e.g.,  $TiAl$ ), resulting in the formation of  $Al_3Ti$  as the predominate reaction product.

There are, however, two more thermodynamically stable aluminide compounds,  $Ti_2Al_3$  and  $Ti_3Al$ . The thermodynamic properties of these compounds, unfortunately, are not in most published thermochemical

data bases (including HSC). Despite these limitations the conclusion of the thermodynamic analysis is that the aluminothermic reduction of  $TiCl_4$  to form  $TiAl$  is feasible.

### Experimental

A fluidized bed reactor was designed to react Al powder with gaseous  $TiCl_4$ . A schematic of the reactor is shown in Figure 3. Simply, a fluidized bed suspends a mixture of particles in an upwardly flowing gas stream. The fluidized bed reactor utilized for the present investigation was designed to react a fixed amount of Al in the bed with a constant source of  $TiCl_4$  flowing through the gas stream. Initially, there will be an excess of Al in the bed relative to the  $TiCl_4$ ; and thus,  $Al_2Ti$  should form as predicted in Figure 2, even at elevated temperatures. As an experiment progresses and the  $Al_2Ti$  is consumed forming aluminides, the relative amount of pure Al to  $TiCl_4$  in the reactor decreases and conversion to  $TiAl$  is predicted.

Experiments were performed in a small (420x30 mm) quartz tube reactor. Because quartz is transparent, visible observations of the powder bed were possible; therefore, easy adjustments to the flow of gas through the reactor to facilitate fluidization of aluminum powder could be made. Typically, the bed was bimodal mixture of 1 gram of 60  $\mu m$  Al powder and 2 grams of 400  $\mu m$  Al powder. This powder mixture was selected because it was found to fluidize quite readily. Argon was used as an inert carrier gas for flowing the  $TiCl_4$  through the reactor. An experiment began by fluidizing aluminum powder with Ar. When the reactor

reached the desired temperature, gaseous  $TiCl_4$  was introduced into the Ar by passing the Ar stream over boiling  $TiCl_4$ . ( $TiCl_4$  boils at 136°C).

Experiments were performed at 600°C and 740°C. The reactor was run at temperature for about 1 hour. Prior to heating to 740°C, the Al was fluidized with an Ar and  $TiCl_4$  mixture at 400°C for 20 minutes. The  $TiCl_4$  flow was stopped and the reactor was heated from 400 to 740°C with only pure Ar flowing through the reactor. When the reactor reached temperature, the  $TiCl_4$  flow was restarted. This sequence prevented the melting of the Al upon heating above 660°C; hence, the experiments occurred in the solid-state and correspond to reactions between  $TiCl_4$  and Al or  $Al_2Ti$ . The resultant powder was analyzed by standard powder X-ray diffractometry.

### Results and Discussion

At 600°C, the Al powder transformed to  $Al_2Ti$  and  $Al_3Ti_2$  (Figure 4). Present in trace amounts (e.g., < 10 percent) were unreacted Al and several titanium-chloride and aluminum-chloride phases (in the diffraction pattern in Fig. 4 an aluminum-chloride hydrate,  $AlCl_3 \cdot 6H_2O$ , is shown). These results correlated well with the prediction of the thermodynamic analysis, that is a combination of  $TiAl$  and  $Al_2Ti$  should form. Clearly, the discrepancy that  $Al_2Ti_2$  formed instead of  $TiAl$ , is a failure of the thermodynamic analysis due to the lack of data for  $Al_2Ti_2$ . Al was also present in trace amounts, this was probably due to the large Al particles (400  $\mu m$ ) in the fluidized bed not fully reacting.

The product removed from the reactor after operating at 740°C was, first, leached in water to remove the chlorides. The product was then passed through a 150 mesh screen (100  $\mu m$  opening) to separate the fine (60  $\mu m$ ) powders from the coarse (400  $\mu m$ ) powders of the bed. The fine powders (those that passed through the screen) consisted of a combination of  $TiAl$  and  $Ti_2Al_3$  (Figure 5). However, X-ray diffraction revealed that the coarse powder (those that did not pass through the screen) consisted of primarily  $Al_2Ti$  with a trace amount of  $TiAl$ .

The experiments were designed to operate in the solid state. The higher Ti-content aluminide phases formed from the reaction of  $TiCl_4$  with the immediate lower Ti-content aluminide phase, or in other words,  $TiAl$  formed from  $TiCl_4$  reacting with  $Al_2Ti$ . The reaction sequence was follows:



The transformation along this chain will be influenced by the reaction kinetics associated with both the dissociation

Figure 3. Schematic of the fluidized bed reactor.

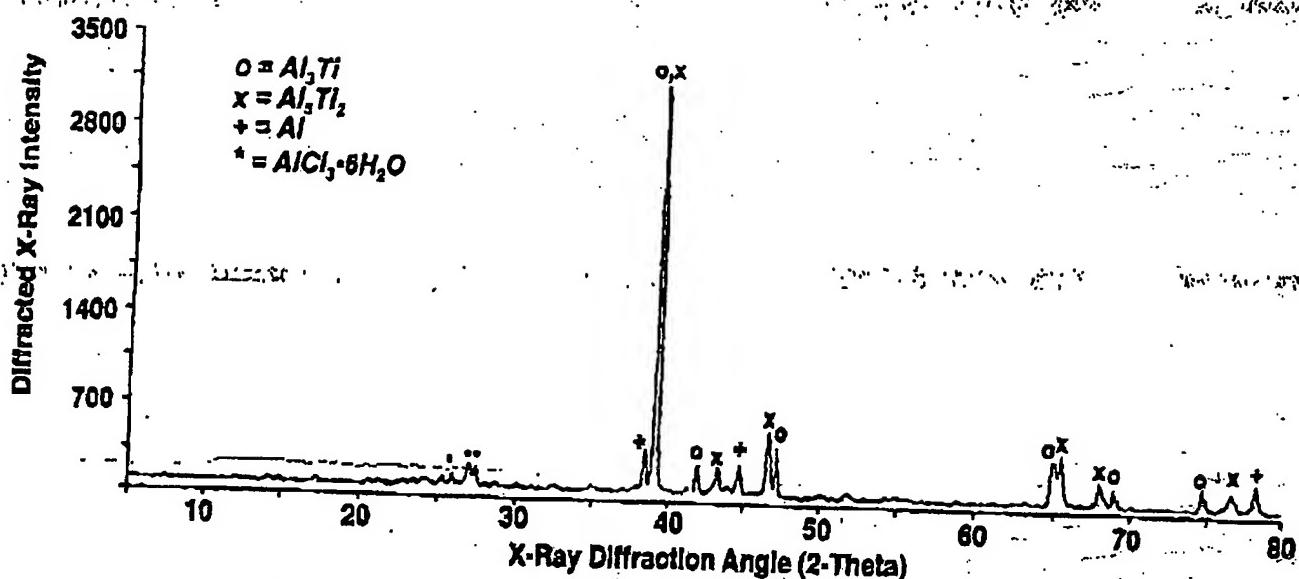


Figure 4. X-ray diffraction scan obtained on Al powder reacted with  $TiCl_4$  at  $600^\circ C$ .

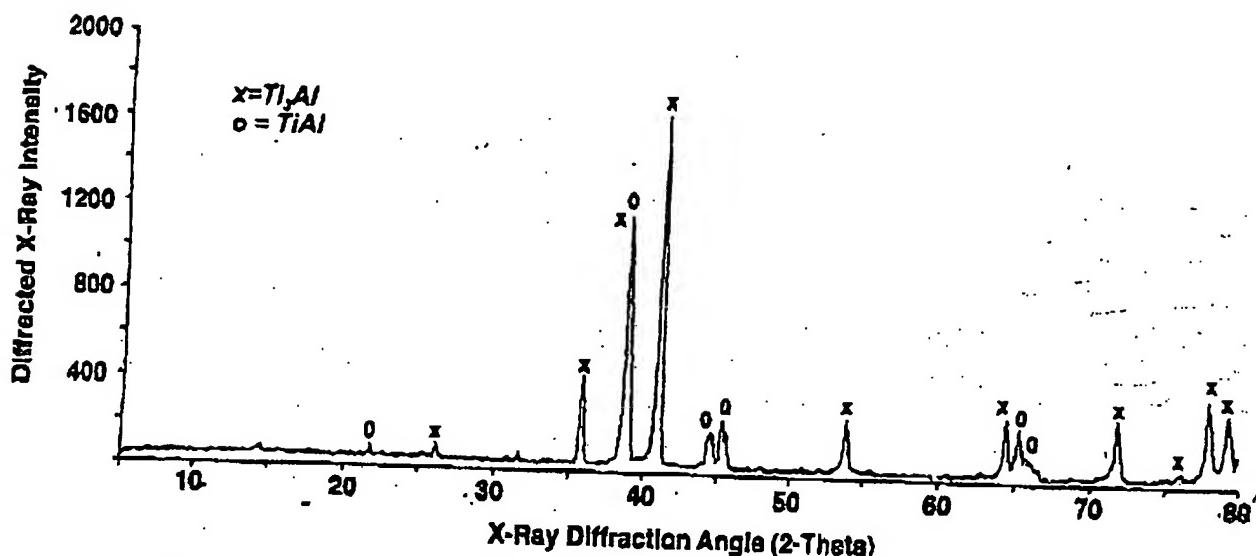


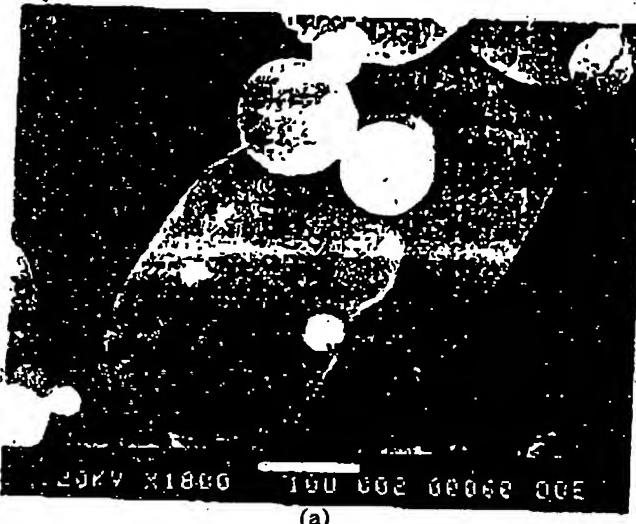
Figure 5. X-Ray diffraction scan obtained on fine ( $40\mu m$ ) Al powder reacted with  $TiCl_4$  at  $740^\circ C$ .

of Ti from  $TiCl_4$  and the diffusion of Ti and Al through any intermediate reaction product (such as  $Al_3Ti$ ). Hence, the coarse ( $400\mu m$ ) Al particles were not held at  $740^\circ C$  for a long enough time period to convert past  $Al_3Ti$ . Whereas, 1 hour at  $740^\circ C$  was sufficient to convert the  $60\mu m$  Al to  $TiAl$  and  $Ti_3Al$ .

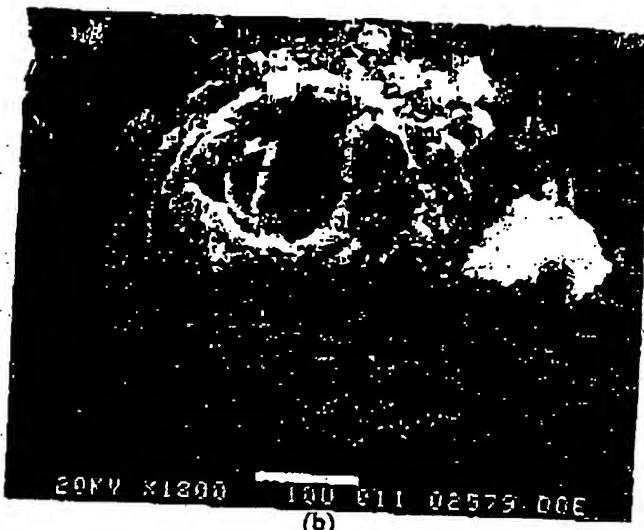
Figure 6 reveals the morphology of the fine  $TiAl$  powder produced by reacting  $740^\circ C$ . Clearly, the morphology of the  $TiAl$  powder is quite different from the starting helium atomized Al powders (compare Figure 6a with Figure 6b).

The morphology of the  $TiAl$  powder is characteristic of powder produced by chemical synthesis techniques.

Clearly, it is possible to make  $TiAl$  by reduction of  $TiCl_4$  by Al. However, the formation of a uniform product will require precise control of the operating conditions (e.g., temperature and  $TiCl_4/Al$  ratio), which was not possible with the experimental apparatus utilized in these initial experiments. Further, the characteristics of the fluidized bed (e.g... powder size and shape), will also influence the reaction products.



(a)



(b)

Figure 6. SEM Micrographs of: (a) the starting Al powder; and (b) the TiAl powder produced by reacting at 740°C

A potential benefit of the direct formation of TiAl from  $TiCl_4$  is the economics of this process. Based on a cost of \$0.60 per pound for aluminum and \$0.48 per pound for  $TiCl_4$ , the cost of raw materials for a pound of TiAl is \$1.64. By contrast the cost of raw materials for producing TiAl from Ti and Al is \$3.50 per pound (using a price of \$5.00 per pound for titanium sponge). Many commercial chemical processes utilize fluidized bed reactors. Hence, the technology exists for the solid-state product of TiAl from  $TiCl_4$  and Al powders on an industrial scale. Further, gas-atomized Al powder is readily available. Hence, it may be feasible to modify the atomization process to react molten Al with a gaseous mixture containing  $TiCl_4$ , and produce TiAl directly during powder atomization. Since, the industrial infrastructure for processing readily exists today (no new technology is required) and the cost of raw material is about half that of conventional melt methods; the Al reduction of  $TiCl_4$  has the potential for being a low cost method for producing TiAl.

#### Summary and Conclusions

The feasibility of producing TiAl directly from  $TiCl_4$  and Al was demonstrated. At temperatures below 600°C, the primary reaction product will be  $Al_3Ti$ . At temperatures above 600°C, it is feasible to convert Al to higher-titanium content aluminide phases. Fine ( $60\mu m$ ) Al powders were

converted to a combination of TiAl and  $Ti_3Al$  in a fluidized bed reactor operating at 740°C for 1 hour. For uniform product formation, precise control over the reaction conditions is required.

#### Acknowledgment

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(54) METHOD OF MAKING ELEMENTAL MATERIALS AND ALLOYS

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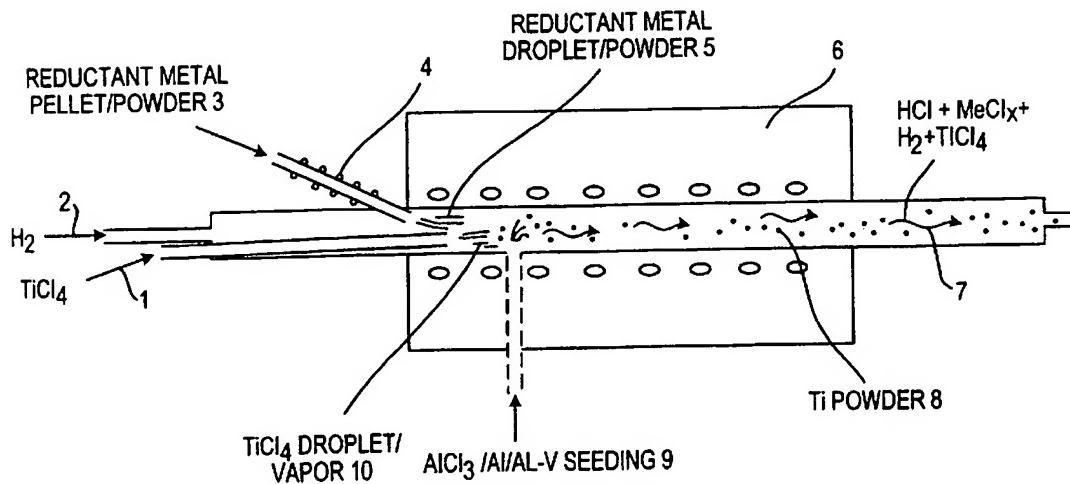
## (57) ABSTRACT

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(21) Appl. No.: 10/242,916

A method of producing an elemental material or an alloy thereof from a halide or mixtures of halides is provided. The halide or mixtures thereof are contacted with a reducing gas in the presence of reductant material, preferably in sufficient quantity to convert the halide to the elemental material or alloy and to maintain the temperature of the reactants at a temperature lower than the boiling point of the reductant material at atmospheric pressure or the sintering temperature of the produced elemental material or alloy.



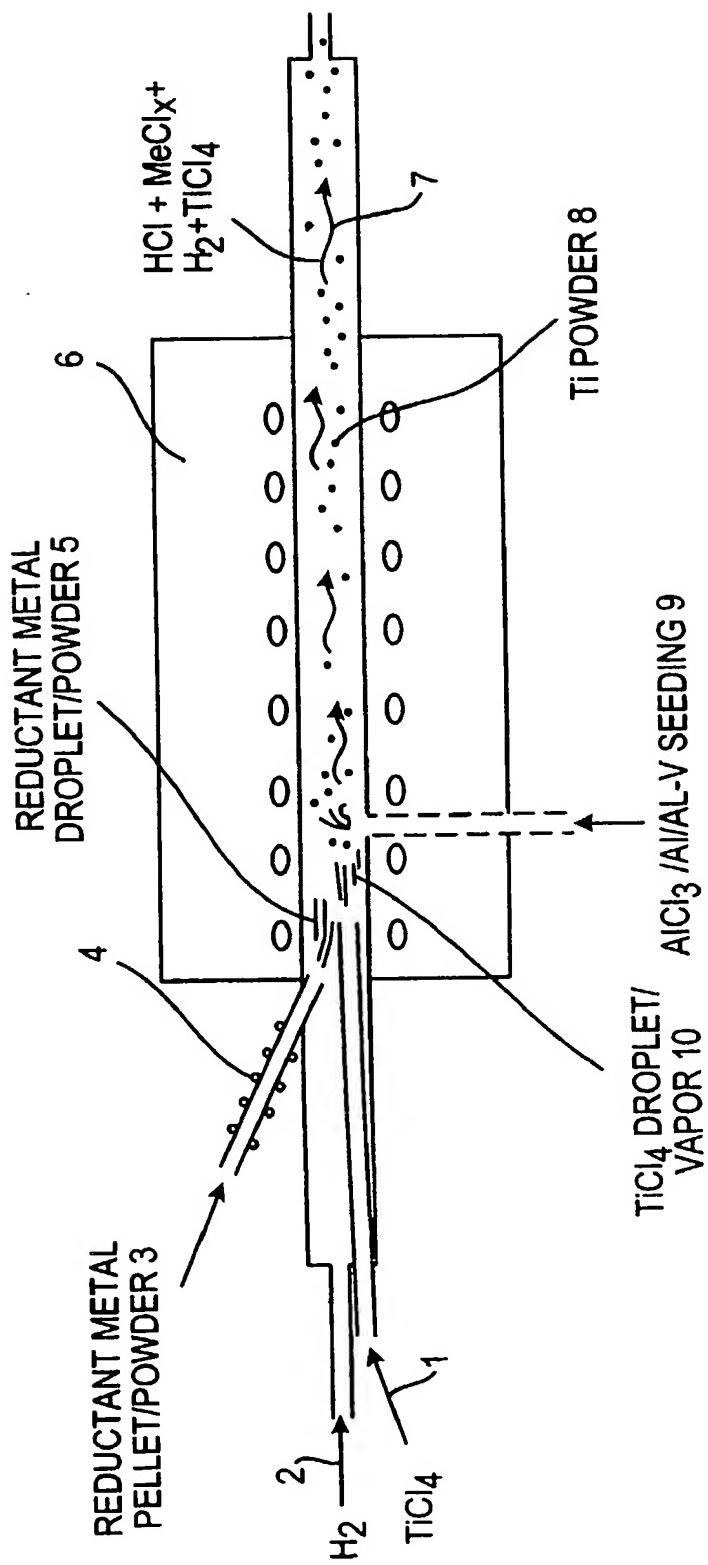


FIG. 1

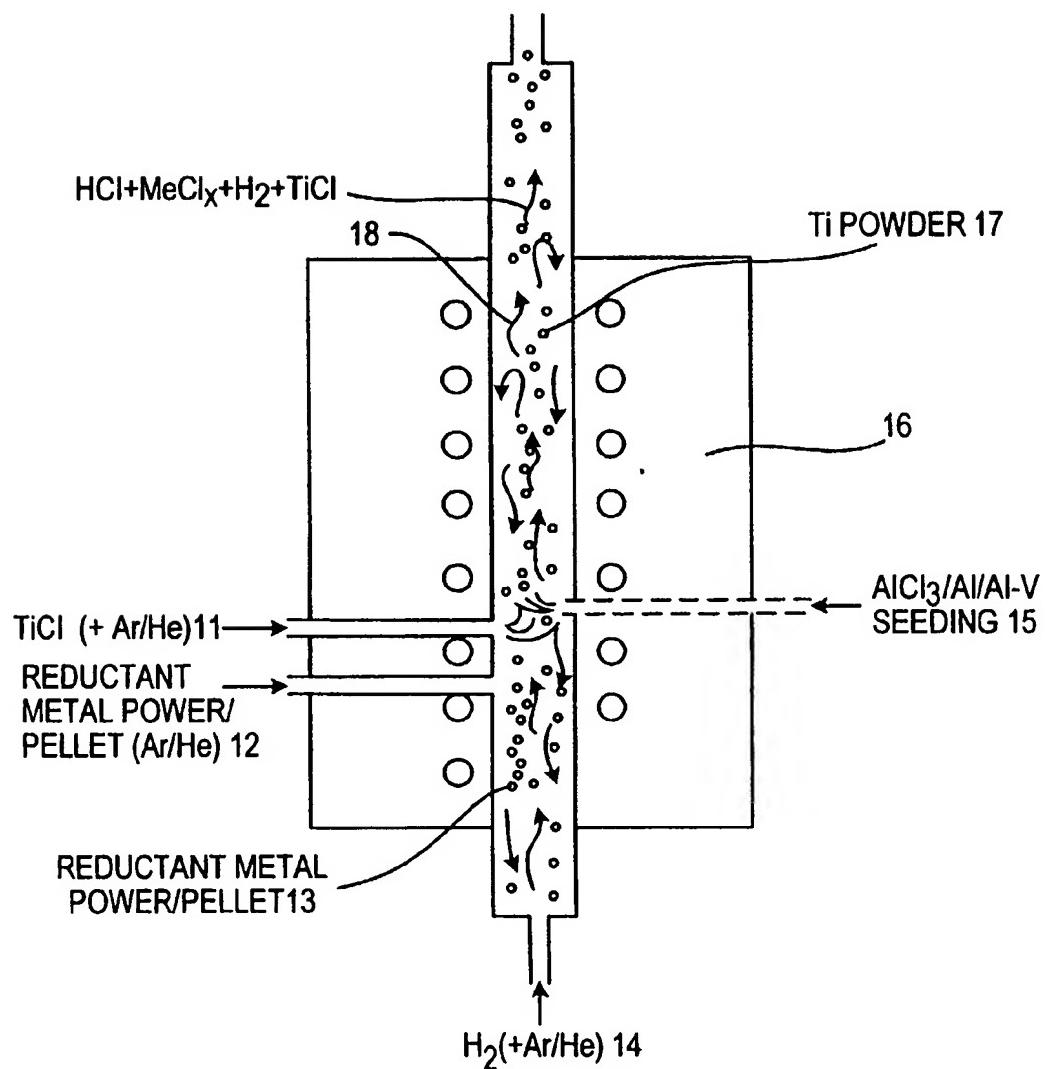


FIG. 2

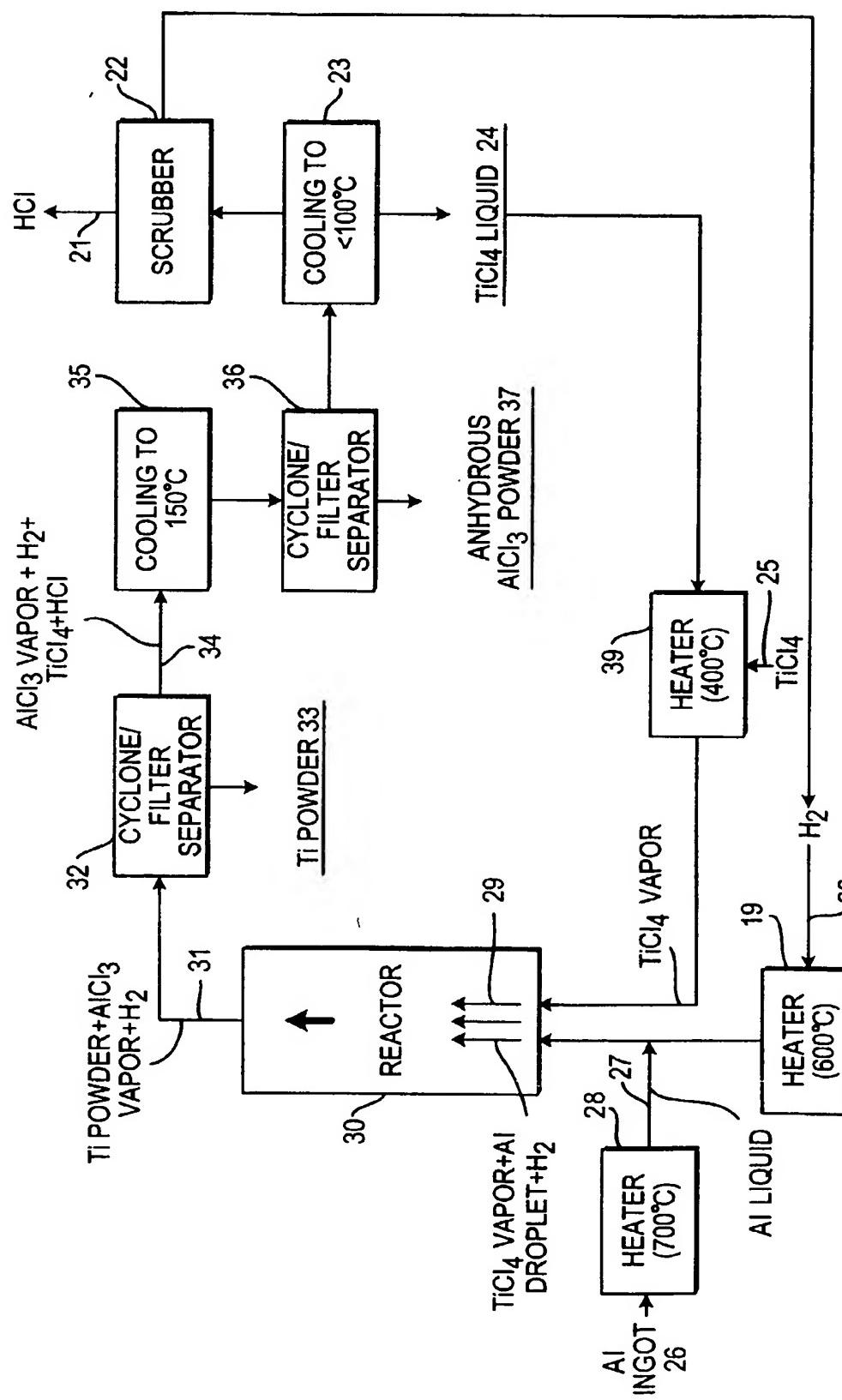


FIG. 3

## METHOD OF MAKING ELEMENTAL MATERIALS AND ALLOYS

### FIELD OF THE INVENTION

[0001] The present invention relates to the field of the production of elemental materials and alloys.

### BACKGROUND OF THE INVENTION

[0002] Often it is desirable to obtain substances in their elemental forms or high quality alloys of these substances in order to use them in certain high-end applications, for example, sports and leisure activities. However, in nature most substances are not readily accessible in their elemental forms.

[0003] For example, frequently titanium occurs in ores as a dioxide or mixed oxide with iron. Because of titanium's affinity for gases and most metals in the periodic table, it is quite difficult to extract elemental titanium from its ores. Consequently, in order to obtain elemental Ti, complex and now well-known processes have been developed. Unfortunately, these processes, as well as similar processes for obtaining other elemental materials can be cumbersome and costly.

[0004] Many naturally occurring substances either exist as halides or are easily converted into halides. These halides may be reduced to their elemental forms by any one of a number of well-known processes. For example, titanium tetrachloride ( $TiCl_4$ ) may be reduced to Ti through the use of reducing agents such as hydrogen, carbon, sodium, calcium, aluminum or magnesium.

[0005] Methods for reducing halides in order to obtain elemental materials have been developed for both batch and continuous processes. One example of a method for the reduction of a precursor material in a batch process is the magnesium reduction of titanium tetrachloride to produce elemental titanium. Unfortunately, the product of this type of batch process requires significant material handling, which provides opportunities for contamination and variation in quality from batch to batch. Consequently, a significant amount of effort has been directed toward developing continuous reduction processes.

[0006] Several different continuous processes for producing elemental materials have been developed. For example, it is known to use Na to reduce  $TiCl_4$  to Ti powder at a temperature of between 350 and 800° C. This process can efficiently produce Ti powder from  $TiCl_4$  at a reasonable cost. Thus, it has high commercialization potential. However, the product Ti powder has a relatively high oxygen concentration, which causes powder sintering. Further, in this process there is an undesirable cumbersome step of separating the Ti powder from Na. Still further, Na can be costly, is of limited supply and must be handled carefully.

[0007] Another method for reduction of a precursor material, for example, for the production of titanium, uses plasma technology to change the thermodynamics of the elemental Ti formation by vaporizing and ionizing it. However, due to the high melting temperature of titanium metal, most plasmas operate at temperatures of above 4000° C. Therefore, the high energy consumption and the limited refractory material availability render this process expensive.

[0008] Another known method involves the use of an electron beam to produce Ti powder. This process is conceptually similar to a plasma process, that is, by utilizing the high temperature from an electron beam, one may produce Ti powder. Unfortunately, this process also consumes a great deal of energy and can be costly.

[0009] Still another known method uses mechanochemical technology to produce Ti powder. In this process,  $TiO_3$ ,  $TiCl_4$  and  $CaH/MgH$  are first milled to produce  $TiH+CaO/CaCl_2$  at temperatures from room temperature to 700° C. Then,  $TiH$  is annealed in a vacuum to produce Ti powder. This process is still in the early stage relative to industrial utilization, and thus far, it appears that the products of this method may suffer from being impure and having slow reaction rates.

[0010] In addition to these processes, it has long been known to produce spongy Ti by electrolysis of  $TiO_2$  in a fused salt bath. In one known process,  $TiO_2$  is directly electrolyzed in fused  $CaCl_2$  at approximately 950° C. to produce a Ti sponge, and the sponge is converted to a powder. Unfortunately, due to the limitations of current technology, it is difficult, if not impossible, to avoid oxygen contamination on the product since the Ti sponge is produced on the surface of  $TiO_2$ .

[0011] The aforementioned methods all suffer from being unable to produce sufficiently pure elemental materials in a sufficiently economical manner. Because of the limitations of these methods, the ability to produce high quality alloys containing these elemental materials is also limited. The present invention provides a solution to these problems by providing methods for economically producing sufficiently high quality elemental materials and alloys.

### SUMMARY OF THE INVENTION

[0012] The present invention is directed to the production of elemental materials and alloys of those materials from the halide precursors thereof, and provides methods for producing elemental materials and alloys of metals and non-metals. The elemental materials and alloys may, for example, comprise Al, As, Sb, Be, B, Ta, Ge, V, Nb, Mo, Ga, Ir, Rh, Os, Ru, Pt, Pd, Ti, U or Re. Preferably, according to the methods for producing these materials, accompanying the reduction of the halide precursor is the production of a significant amount of heat.

[0013] In one embodiment, the present invention provides a method of producing an elemental material, said method comprising:

[0014] (a) combining a precursor material with a reducing gas to form an elemental material and a first reaction product, wherein said precursor material comprises a halide of an elemental material; and

[0015] (b) exposing said first reaction product to a reductant material to form a reductant-halide.

[0016] Under this embodiment, typically the first reaction product will be a gas or vapor, while the second reaction product is a solid, liquid, gas or mixture thereof, and the concentration of the first reaction product is controlled by the formation of the reductant-halide.

[0017] In a preferred embodiment, the present invention provides a method of producing Ti, said method comprising

introducing  $TiCl_4$  in the form of a vapor or droplet to  $H_2$  to produce Ti and HCl, and exposing the HCl to a reductant solid or liquid selected from the group consisting of Al, Mn, Mg, Na, Ca, K, Li, Ba Be, Ce, Cs, Hf, Pa, Rb, Sr, Th, U, and Zr.

[0018] In a second embodiment, one may form an alloy by using a seed material in connection with the first embodiment.

[0019] In a third embodiment, the present invention provides a method for producing an alloy by combining more than one precursor material with a reducing gas to form an alloy material and one or more first reaction products. The one or more first reaction products are in turn exposed to a reductant material.

[0020] The present invention can be used in batch or continuous processes. However, the present invention is particularly beneficial when used in continuous processes. Accordingly, the present invention provides methods for producing elemental materials and alloys through continuous processes that have capital and operating cost advantages over existing technologies.

[0021] Additionally, the present invention is particularly beneficial in connection with reduction reactions that produce elemental materials and alloys from the exothermic reduction of precursor materials, and preventing the substances that are produced from sintering onto the apparatuses used to produce them. In addition to providing methods for producing elemental materials and alloys thereof, the present invention provides a means for recovering and reusing the reducing gas, thereby substantially reducing the environmental impact of the process.

#### BRIEF DESCRIPTION OF THE FIGURES

[0022] FIG. 1 is a representation of the titanium tetrachloride and reductant-metal injection reactor of continuous titanium powder production by hydrogen and reductant materials.

[0023] FIG. 2 is a representation of the fluidized-bed reactor of continuous titanium powder production by hydrogen and reductant materials.

[0024] FIG. 3 is a representation of the processing steps of continuous titanium powder production by hydrogen and reductant materials.

#### DETAILED DESCRIPTION OF THE INVENTION

[0025] According to the present invention, a precursor material or a set of more than one precursor materials is exposed to a reducing gas to yield a metal, non-metal or alloy and one or more first reaction products. The one or more first reaction products are exposed to a reductant material to form a reductant-halide or reductant-halides. The combination of these steps enables the precursor material or set of more than one precursor materials to be converted efficiently into an elemental material or an alloy.

[0026] The present disclosure is not intended to be a primer on the formation of elemental materials or alloys. Readers are referred to appropriate available texts for background on these subjects.

[0027] According to one embodiment of the present invention, an elemental material is produced through a two-step process. An "elemental material" is a substance that is present in its elemental form, e.g., Ti or Co, as opposed to in its ionic form or as part of a chemical compound. Thus, it has a valence of 0.

[0028] First, a precursor material is converted by a reducing gas into an elemental material. At the same time, a by-product comprising a halogen moiety and the element or elements of the reducing gas is formed. This reaction is the "first reaction."

[0029] Second, the aforementioned by-product of the first reaction, which is referred to as a "first reaction product," reacts with a reductant material both to form a new substance comprised of the halide of the reductant, and to re-form the reducing gas. This reaction is the "second reaction." Preferably, there is sufficient manipulation of mixing and turbulence of the gas or vapor in the system such that they are strong enough to ensure that the concentration of the corresponding first reaction product is controlled by the second reaction. Thus, the formation of the elemental material is executed in the first reaction, and due to thermodynamics, is driven by the second reaction.

[0030] The precursor material will preferably be a metal or non-metal halide. The halogen within the precursor material may for example be Cl, Br, F or I or a combination thereof, but is preferably Cl, Br, F or a combination thereof. Further, preferably, the precursor material comprises a halide of at least one substance selected from the group consisting of Ti, Al, As, Sb, Be, B, Ga, Ge, Mo, Nb, Ta, Zr, V, Rh, Ir, Os, Ru, Pt, Pd, Re and U. Examples of precursor materials include, but are not limited to  $TiCl_4$ ,  $VCl_4$ ,  $NbCl_5$ ,  $MoCl_4$ ,  $GaCl_3$ ,  $UF_6$  and  $ReF_6$ . Further, the precursor material is preferably in the form of a vapor or droplet, referred to herein as a "halide vapor or droplet." If the precursor material is not in the form of a vapor or droplet, preferably, it will be converted into a vapor or droplet.

[0031] Methods for converting a precursor material into a vapor or droplet are well-known to persons skilled in the art, and include but are not limited to dissolving the precursor material in a solvent and heating the solution or exposing it to an already heated gas.

[0032] The precursor material may be introduced into an environment that contains the reducing gas by, for example, submerging the precursor material in the reducing gas through an injector. Preferably, the injector will comprise a nozzle. The precursor material may be added to the reducing gas under conditions in which the gas is static or flowing; however, it is preferable to introduce the precursor material to the reducing gas when the reducing gas is a continuous stream.

[0033] The reducing gas reduces the precursor material to the elemental material. This first reaction is preferably exothermic, though as is well known to persons skilled in the art, the kinetics of the reduction for different reducing gases and/or different halides will be different.

[0034] The reducing gas may, for example, comprise one or more substances selected from the group consisting of  $H_2$ ,  $H_2S$ ,  $NH_3$ ,  $CH_4$ ,  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$ ,  $CH_3NH_2$ ,  $CH_3SH$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_2H_5Cl$ ,  $C_3H_4$ ,  $C_3H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_4H_8$ ,  $C_5H_{12}$ ,  $CF_4$ ,  $CF_3C_1$ ,  $CF_2Cl_2$ ,  $CFCl_3$ ,  $CHF_3$ ,  $CHF_2Cl$ ,

$\text{CHFCl}_2$ ,  $\text{CF}_3-\text{CF}_3$ ,  $\text{CF}_3-\text{CF}_2\text{C}_1$ ,  $\text{CF}_2\text{Cl}-\text{CFCl}_2$ ,  $\text{D}_2$ ,  $\text{B}_2\text{H}_6$ ,  $\text{GeH}_4$ , and  $\text{SiH}_4$ . When  $\text{TiCl}_4$  is to be reduced, preferably the reducing gas is  $\text{H}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ , or  $\text{NH}_3$ .  $\text{H}_2$  is particularly preferable because it is clean, abundant, and relatively inexpensive.

[0035] Depending on the particular reducing gas or combination of reducing gases that is used, combining a particular precursor material with the reducing gas may generate one or more different first reaction products.

[0036] Optionally, the precursor material may be introduced to the reducing gas by being transported by a carrier gas. By way of example, any of the substances identified above as reducing gases may serve as carrier gases. Thus, the precursor material may be transported by a carrier gas that is the same chemical species as or a different chemical species than the reducing gas and then combined with or submerged in the reducing gas. Alternatively, the precursor material may be combined with an inert gas alone such as  $\text{He}$ ,  $\text{Ar}$ , or  $\text{N}_2$ , which will serve as a carrier gas, and then combined with the reducing gas. When  $\text{TiCl}_4$  is to be reduced, preferably the inert gas is  $\text{Ar}$  or  $\text{He}$ . In one embodiment, the carrier gas comprises both one of the aforementioned gases that are described as reducing gases and an inert gas.

[0037] After the first reaction begins and a first reaction product has been produced, the reductant material will react with the first reaction product and reduce and control its concentration in the system. The two reactions may occur simultaneously, instantaneously or sequentially. In this "second reaction," the reductant is preferably a solid, for example, a powder or pellet, or a liquid. For  $\text{TiCl}_4$  reduction, by way of example, the reductant may be one or more substances selected from the group consisting of metals such as  $\text{Al}$ ,  $\text{Ba}$ ,  $\text{Be}$ ,  $\text{Ca}$ ,  $\text{Ce}$ ,  $\text{Cs}$ ,  $\text{Hf}$ ,  $\text{K}$ ,  $\text{Li}$ ,  $\text{Mg}$ ,  $\text{Mn}$ ,  $\text{Na}$ ,  $\text{Pa}$ ,  $\text{Rb}$ ,  $\text{Sr}$ ,  $\text{Th}$ ,  $\text{U}$  and  $\text{Zr}$ ; and non-metals such as the oxides  $\text{CrO}_2$ ,  $\text{CsO}_4$ ,  $\text{KO}_2$ ,  $\text{KO}_4$ ,  $\text{NaO}_3$ ,  $\text{NaO}_4$ ,  $\text{RbO}_4$ ,  $\text{UO}_2$ , and  $\text{VO}$ . The specific reductant solids or liquids that may be used in a particular application to reduce the product of the reducing gas and precursor material will, as discussed below, depend on the chemical and physical properties of the precursor material that is selected.

[0038] When there is sufficient excess of the reductant material over the stoichiometric quantity needed to react with the first reaction product, the temperature of the powder non-metal or metal that is produced may be controlled to prevent the powder from depositing on the equipment. Preferably, the reductant material will, based on stoichiometry, be present in greater than 6% excess relative to the first reaction product. As with the reducing gas, the reductant too may be added through a nozzle and in a continuous stream.

[0039] The reductant metal or non-metal is selected such that it forms a more stable halide material (the "second reaction product" or "reductant-halide") than the precursor material. The reductant-halide may be a solid, liquid, gas or mixture. However, it is important that the reductant-halide has a lower or more negative free energy of formation than the precursor material under the selected operating conditions. One may use more than one reductant material in a given system, though if more than one reductant is used, preferably each reductant forms a halide with lower formation free energy than the precursor material or materials that are reduced.

[0040] The above-described first reaction and second reaction may occur in one reactor, such as in a fluidized bed, or under conditions that prevent the precursor material from contacting the reductant material, such as in separate but gas permeable reactors or chambers that permit vapor to travel between them, and the concentration (or amount) of at least one of the products from the first reaction is controlled by the second reaction. During the combining of the precursor material with the reducing gas and optional carrier gas, one preferably maintains a sufficient turbulence or mixing in order to ensure an effective reaction of the first reaction product with the reductant material in the second reaction, and the concentration of the first reaction product in the system is controlled by the second reaction. Preferably, the precursor material is contacted with or submerged in a stream of reducing gas in the presence of the reductant material.

[0041] After the elemental material is formed, it should be separated from the other substances. Because there are two reactions that take place, under carefully controlled conditions, the elemental material and the reductant will not come into contact with each other regardless of whether being present in the same reaction vehicle. And more important is that the reductant-halide product will preferably not be formed on the surface of the elemental material. In these circumstances, the produced elemental material will be a powder that is not contaminated by the reductant or the reductant-halide. Consequently, the elemental material may easily be separated on the basis of methods known to persons skilled in the art for separating materials based on size and/or density, including but not limited to filtering and cycloning.

[0042] For example, one may use  $\text{H}_2$  as the reducing gas, which under the preferred operating conditions of the present invention will cause the first reaction product to be gaseous  $\text{HCl}$ . Under these conditions, the  $\text{HCl}$  is easily separated from the  $\text{Ti}$  powder and will be able to react with the reductant material to form the reductant-halide; the formed reductant-halide is not physically (or mechanically) trapped by the  $\text{Ti}$  powder. By way of an additional example, one may use  $\text{Al}$  as the reductant to produce  $\text{Ti}$  from titanium tetrachloride.  $\text{Al}$  has a low boiling point, and  $\text{AlCl}_3$  will be a vapor under preferred operating conditions. Thus, the  $\text{Ti}$  powder would be easily separated from the  $\text{AlCl}_3$ .

[0043] Further, the reductant-halide and re-formed reducing gas may be separated into constituent parts. The re-formed gas may be reused for the process described above or used to reduce other substances or in other applications in which such gases may be used. Similarly, the reductant-halide can be recovered and used.

[0044] Due to the limitations of most operating conditions, there may be some amount of unreacted precursor materials and first reaction products that will need to be treated or further processed. Recovered unreacted reductants may be used to treat these or additional first reaction products.

[0045] In one preferred sub-embodiment,  $\text{Ti}$  powder is produced according to the above-described method. When forming  $\text{Ti}$  powder, the  $\text{Ti}$  powder may be nucleated from the gas phase, if the thermodynamic driving force is great. Preferably, in generating the  $\text{Ti}$  powder, one uses a relatively large size reductant powder, pellet or droplet. This permits the newly produced smaller titanium to be carried to a

further downstream area in a continuous-process injection reactor or to be carried out from the top in a fluidized-bed reactor, where it is easily separated and recovered.

[0046] Although not wishing to be bound by any one theory, it is believed that the benefit of the present invention is possible by forming one or more reductant-halides in the second reaction that have lower formation free energies (also referred to as larger negative formation free energies) than the precursor materials, when stoichiometric equivalents are compared.

[0047] As is well known to persons skilled in the art, precursor materials that contain halides may be reduced in the presence of a reducing gas such as hydrogen. For example, titanium tetrachloride may be reduced in the presence of hydrogen to form elemental titanium and hydrochloric acid. However, typically reactions such as these are not favored thermodynamically and must be carried out at elevated temperatures.

[0048] The thermodynamics of a reaction is reflected in the Gibbs free energy of the reaction. Exemplary standard Gibbs free energies are provided in Table I below for both  $TiCl_4$  and other chlorides that represent potential reductant-halide compositions, as well as precursor materials in and of themselves.

[0049] The reaction of Ti with  $H_2$  is provided below in Formula I:



[0050] According to the present invention, by causing the halide product of this type of reaction, to enter a second reaction that forms a product with a lower formation free energy than the initial precursor material, the first reaction will be continuously driven to the right in order to compensate for the removal of the halide product of the first reaction. Due to thermodynamics, this will enable the first reaction to be carried out under a lower temperature, and thus be more cost-effective.

[0051] As is implied by this theory, for a given precursor material, it is important to select a reductant for which the product has a lower formation free energy than the precursor material and thus forms a more stable reductant-halide than precursor halide to drive the first reaction. If this is not the case, it will not drive the reaction described in Formula I to the right.

[0052] For a selected precursor material, the reductant material that can effectively facilitate reduction to the elemental material will be thermodynamically independent of the reducing gas. Thus, changing the reducing gas will not affect the selection of the reductant material from the point of view of thermodynamics, though it will affect the rate of the reaction via kinetics.

[0053] For example, if one were to continue with the reaction described above, one could use a metal such as Al, Mn, Mg, Na or Ca to generate a metal chloride and gaseous hydrogen. If one were to select Na, the reaction would be represented by Formula II:



[0054] As is reflected in Formula II, the elemental material, in this case the titanium described in Formula I, does not appear. In this second reaction, hydrogen gas is regenerated

and sodium chloride is formed. More Ti is formed in response to the removal of Na, but its chemical form will not change. One additional benefit is that the hydrogen gas is regenerated and can be reused, while the amount of hydrochloric acid that will be produced is reduced.

[0055] The function of hydrogen in the overall  $TiCl_4$  reduction reaction is like a catalyst. But to be exact, hydrogen is not a catalyst in the reaction because it is a reactant of the primary reaction and then a product of the second reaction. The participation of  $H_2$  in the two reactions also greatly reduces the difficulty of the separation and increases the quality of the product because there is no physical trapping between the produced elemental material and the reductant-halide.

[0056] The above-described process preferably takes place at a temperature that is sufficiently low that the elemental material that is produced is quenched by contact with the reductant solid or liquid. Additionally, it is preferably below the sintering temperature of the elemental material. Moreover, it is desirable though not necessary to be able to run the reaction at atmospheric conditions.

[0057] FIG. 3 demonstrates a flow chart of one embodiment of this process. According to this process,  $TiCl_4$ , 25, may be heated, for example at 400° C. by a heater, 39, to form a  $TiCl_4$  vapor. This material is sent to a reactor, 30. Also sent to the reactor is  $H_2$ , 20, that has been heated at for example, 600° C., 19, and an Al ingot, 26, that has been heated at for example, 700° C., 28, to form an Al liquid, 27. Thus, Al droplets,  $H_2$  gas and  $TiCl_4$  vapor will enter the reactor, 29.

[0058] The  $TiCl_4$  is reduced, and  $AlCl_3$  vapor, Ti and  $H_2$  are formed, 31. These products are sent to a cyclone or filter separator, 32, and Ti powder may be recovered, 33.  $AlCl_3$  vapor,  $H_2$  and residual  $TiCl_4$  and HCl, 34, are sent to a cooling stage, 35, where the substances are cooled to a temperature of approximately 150° C. Following this stage, there may be another cyclone or filter separator stage, 36, that permits the recovery of anhydrous  $AlCl_3$  powder, 37. The other substances may be sent to another cooling stage, for example a cooling apparatus that cools the products to less than 100° C., 23, which will permit recovery of  $TiCl_4$  in the form of a liquid, 24, which can be reheated, 39, and returned to the reactor. The hydrogen containing substance may be sent to a scrubber, 22, and HCl, 21, may be sent for waste treatment, while  $H_2$ , may also be sent back to the reactor.

[0059] Under different circumstances that may, for example, be dictated by limitations of equipment, one may choose to vary some of the operating conditions such as using a vapor or droplet as a source of the elemental precursor and varying the operating temperatures and pressures. For example, under one process of the present invention, one may use droplets of  $TiCl_4$ ,  $H_2$  gas, and Al powder to generate Ti powder and a solid  $AlCl_3$  by operating at <130° C. and at ambient pressure. Alternatively, one may use  $TiCl_4$  vapor instead of  $TiCl_4$  droplets and operate at 130-177° C. and at ambient pressure, which would generate the same products. In still another variation, one may use  $TiCl_4$  vapor,  $H_2$  gas and Al as a mixture of droplets and powder by operating at between 180 and 660° C. at pressures between ambient and 3 atm to generate Ti powder and  $AlCl_3$  vapor. Still further, one may choose to operate at

greater than 660° C. at which temperatures all of the Al would be in the form of droplets, and at either ambient or elevated pressures to generate Ti powder and AlCl<sub>3</sub> vapor.

[0060] From a practical point of view, using a reducing gas such as H<sub>2</sub> in combination with a reductant material is different from using the reductant materials only. Hydrogen changes the TiCl<sub>4</sub> reduction from a heterogeneous surface reaction on the reductant metal surface to a homogeneous gas reaction.

[0061] Almost all heterogeneous surface reactions are limited by surface area, regardless of whether the reaction rate is controlled by surface chemistry or by mass transfer. If a reaction is controlled by surface chemistry, then the reaction rate will be proportional to the surface area. If a reaction is controlled by mass transfer, the reaction rate will be limited by the transportation of either reactant materials to the surface or the reacted products from the surface or both.

[0062] Homogenous reactions are not similarly limited. Consequently, the change to a homogeneous gas reaction will result in a substantial increase in the reaction rate. This is particularly important for the reductant metals that have relatively small thermodynamic driving forces, such as Al and Mn, of which the overall-reaction Gibbs free energy for TiCl<sub>4</sub> reduction are -101,200 and -143,800 J/mol at 298° K, respectively. These small thermodynamic tendencies can more easily be nullified by the activation energies caused by the surface reaction, which leads to the very slow reaction rate or no reaction at all.

[0064] However, if the reduction of TiCl<sub>4</sub> is performed according to the methods of the present invention, there will be two reactions, Formulas V and VI or Formulas V and VII below:



[0065] By using the pairs of reactions represented by Formulas V and VI or Formulas V and VII, the activation energy of the reaction of Formula V is significantly lower than the activation energy to that of Formulas III or IV. Additionally, if one uses excess Al or Mn to increase the surface area the activation energy of reaction of Formula VI or VII can be reduced.

[0066] Further, as persons skilled in the art know, if TiCl<sub>4</sub> is reduced solely by a metal, the newly-born titanium metal and the produced metal halide, most of which is solid or liquid under preferred operating conditions, will form simultaneously on the surface of the reductant metal and be physically trapped by one another. Therefore, one must address how to separate the produced Ti product from the original reductant metal and reductant-halide. By contrast, using H<sub>2</sub> with metals changes the formation process of the titanium powder. The titanium powder can be nucleated from the gas phase and grown on it if the thermodynamic driving force is great enough. Even if when H<sub>2</sub> is used, the thermodynamic driving force is not great for nucleation

TABLE 1

Metals being thermodynamically able for TiCl<sub>4</sub> reduction

Metal	Chloride	$\Delta G^\circ_{298}$ , formation of Chloride (kJ/mol)	T <sub>metal</sub> melt (°C.)	T <sub>metal</sub> boil (°C.)	Temperature Range for Effectively Thermodynamic Reduction* (K)	TiCl <sub>4</sub> Temperature Range	Metal State in
(Ti)	(TiCl <sub>4</sub> )	-737.2	1670				liq
(Ti)	(TiCl <sub>4</sub> )	-726.3		3289			gas
Al	AlCl <sub>3</sub>	-628.8	660.45	2520	600-1800		cry, liq
Ba	BaCl <sub>2</sub>	-810.4	729	1805	300-2500		cry, liq
Be	BeCl <sub>2</sub>	-445.6	1289	2472	300-2500		cry, liq, gas
Ca	CaCl <sub>2</sub>	-748.8	842	1494	300-2500		cry, liq
Ce	CeCl <sub>3</sub>	-977.8	798	3443	300-2500		cry, liq, gas
Cs	CsCl	-414.5	28.39	671	300-2500		cry, liq, gas
Hf	HfCl <sub>3</sub>	-901.3	2231	4603	300-2500		cry, liq
K	KCl	-408.5	63.71	759	300-2500		cry, liq, gas
Li	LiCl	-384.4	180.6	1342	300-2500		cry, liq
Mg	MgCl <sub>2</sub>	-591.8	650	1090	300-2500		cry, liq, gas
Mn	MnCl <sub>2</sub>	-440.5	1246	2062	300-2500		cry, liq, gas
Na	NaCl	-384.1	97.8	883	300-1250		cry, liq, gas
Pa	PaCl <sub>3</sub>	-953.0	1572	—	300-2500		cry, liq
Rb	RbCl	-407.8	39.48	688	300-2500		cry, liq, gas
Sr	SrCl <sub>2</sub>	-781.1	769	1382	300-2500		cry, liq, gas
Th	ThCl <sub>4</sub>	-1094.5	1755	4788	300-2500		cry, liq
U	UCl <sub>4</sub> /UCl <sub>3</sub>	-799.1/-930.0	1135	4134	300-2500		cry, liq
Zr	ZrCl <sub>4</sub>	-889.9	1855	4409	300-2500		cry

\*The Gibbs free energy is calculated and compared in the range of 300 to 2500 K, which is the preferred range of operation, but application will be beyond the range.

[0063] For example, from the thermodynamic calculation, TiCl<sub>4</sub> can be reduced directly by Al or Mn. This reaction is summarized in Formulas III and IV:



under typical operating conditions, seeds can be added. The seeds may be either the same material as the to-be-reduced elemental material, such as Ti, or an easy-to-handle material such as AlCl<sub>3</sub>. For the former type of seed, no separation step is necessary. The latter type of seed can be easily

washed out or vaporized in a relatively low temperature from the titanium powder.

[0067] The means for combining the precursor material with the reducing gas and the reductant material are not limited to any one particular means, and any means that is now known or that comes to be known to persons skilled in the art that would be useful with the present invention may be used. For example, the precursor material may first be submerged in a static or flowing reducing gas and the first reaction product may be exposed to a reductant material in the form of a solid or liquid to form an elemental material and a reductant-halide.

[0068] Under a preferred method, the precursor material and the reducing gas flow continuously through a device such as a nozzle with concentric portions. The elemental material and the reducing gas may flow through the inner nozzle while the reductant material flows through the outer nozzle. Under this embodiment, it will be preferable for the vapor flow to be turbulent.

[0069] In a second embodiment of the present invention, one may use a seed to produce an alloy of elemental materials from a precursor material or to assist in forming the elemental material. According to this embodiment, a precursor material as described above, may be exposed to a reducing gas by for example, submerged injection in the presence of additional metal particles as seeds to reduce the halide on the seeds and to form an alloy with the seed material. As with the prior embodiment, the first reaction product would be contacted with a reductant solid or liquid material.

[0070] During this process, which is preferably a continuous process, for  $TiCl_4$  reduction, the seed may, for example, the one or more of the following, Al, B, Be, Ga, Sb, Ta, Mo, Nb, Sn, Cr, Fe, V, Mg, Na, Mn, Zr, or Ca, and the temperature of the solid or liquid reductant away from where the halide vapor is introduced is preferably maintained in the range of from about -50° C. and 1200° C. Further, the seed may be the same substance as the element, in which case it facilitates the formation of the elemental material, or comprise an element or elements that can form an alloy with the element of the precursor material. Preferably, the seed is a metal that can form a stable alloy with the substance in the precursor material to be reduced.

[0071] The seed is preferably introduced as a particle or droplet through a nozzle, and may be introduced as part of the carrier gas described above. Additionally, the seed preferably possesses an average particle size in the range of 0.1 micrometers to 1 millimeter. When using a seed, the immediate product from the reaction of the precursor material and the reducing gas may be a pre-alloy or elemental blend that may need to be subsequently treated to form an alloy that may be used commercially.

[0072] For example, one may use this method to produce a Ti—6Al—4V. Vanadium cannot effectively reduce  $TiCl_4$  under the preferable operating temperature and pressure. A mixture of fine Al and V powders with a weight ratio of 3/2 for Al and V may be used as seeds, where the Al is in 6% stoichiometric excess relative to  $TiCl_4$ . When this mixture is heated to above 660° C., such as 700° C., Al will become molten and V will stay as particles in the melt because of their different melting points. The melting point for Al and

V are 660 and 1910° C., respectively. If this molten mixture is injected (at the temperature above 660° C., such as 700° C.) into the reactor at a certain speed as seeds, it may turn into individual vanadium particles surrounded with molten Al. If the HCl concentration in the reactor is controlled by adding a stronger-reducing metal (e.g. Mg or Na) the  $TiCl_4$  will be preferably reduced by  $H_2$  but nucleated and grown on the surface of the seeds to form a Ti—6Al—4V alloy or pre-alloy depending on the operating temperature.

[0073] Alternatively, in a third embodiment an alloy may be produced by using more than one elemental precursor in the same reaction system. In this case, if two precursor materials that use the same halogen were used, at least one type of first reaction product would be formed. If different halogens were used then there would be more than one type of first reaction product, in which case collectively there would be "first reaction products." The third embodiment can be used in combination with the second embodiment. Thus, one could use a seed and more than one precursor material.

[0074] In any of the embodiments, the elemental material or alloys thereof may, for example, be produced continuously in a fluidized bed at a certain flow velocity and turbulent pattern. The flow velocity and the pattern is preferably sufficient to keep the precursor material and the reductant material fluidized and the concentration of the first reaction product being controlled by the second reaction, which will depend in part on the parameters of the apparatus selected and the chemical substance used.

[0075] If the quantity of the reductant material is sufficiently in excess of the stoichiometric quantity necessary to reduce the halide vapor for quenching the reaction products below the sintering temperature of the produced elemental material or alloy, it is possible to recover or to remove the heat from the excess elemental material and/or the reductant material. Thus, it is possible, according to the present invention, to produce elemental materials and alloys that do not sinter.

[0076] By way of example, a continuous process reactor may be used for the titanium powder and alloy production, as shown in FIG. 1. In this process,  $TiCl_4$ , 1, may be injected and if not already in the form of a droplet or vapor, be converted into that form, 10, and sent to the reactor chamber where it will quickly react with  $H_2$ , 2, to form Ti powder and HCl. Al (or other corresponding reductant metals or chemicals), 3, may be injected while being exposed to a heater, 4, and combined with the halide droplet or vapor, 5. In the reaction chamber the reductant will reduce and control the HCl concentration by forming  $AlCl_3$  and  $H_2$ . Either droplet or powder of Al may be used depending on the reaction chamber's operating temperature.

[0077] The carrier gases, not shown, may, for example, be Ar or He, depending on the requirement of the  $H_2$  concentration for the reaction and/or price. Optionally, there can be the introduction of seed, by, for example, injection, 9, which would facilitate the nucleation of Ti powder and/or the formation of an alloy.

[0078] The production rate, produced particle size, shape and density will be functions of the reaction thermodynamics and kinetics. They can in part be controlled by reaction temperature, e.g., a furnace, 6. Ti powder, 8, may be

nucleated from the first reaction and grown on the nuclei or the added seeds and leave the reactor with the exhaust gas, including the residual hydrochloride,  $TiCl_4$  and metal chloride, 7.

[0079] A fluidized-bed reactor may also be used for Ti and Ti-alloy powder production, as shown in FIG. 2.  $TiCl_4$  may, for example, be introduced into the system from the middle of the reactor and reduced to Ti powder by  $H_2$  in the gas phase of the upper portion of reactor. The produced Ti powder, which has a relatively small size may be carried out from the top of the reactor by the exhaust gas. The continuous and excess reductant metal pellets with relatively larger size will stay and be fluidized by  $H_2$  (or Ar or He or a mixture thereof) in the bed to react with the HCl and control the concentration of HCl in the reactor.

[0080] Thus as shown in the figure,  $TiCl_4$  in the presence of Ar or He, 11, may be injected into a chamber tube that contains the reducing gas, 14. Similarly, reductant metal powder or pellets may be injected by means of a carrier gas of Ar,  $H_2$  or He or a mixture thereof, 12. Optionally, a seeding material may also be added, 15. The chamber tube may be located within a furnace, 16, which allows one to add heat to the system.

[0081] In the chamber, the  $TiCl_4$  will react to form Ti powder, 17, and HCl. The HCl will react with the reductant to form a reductant chloride and  $H_2$ , which along with the residual  $TiCl_4$  and HCl can be removed by the exhaust gas, 18. Similarly, unreacted reductant will not be carried away with the metal chloride, 13, because of its relative larger particle size. Moreover, even if some small size unreacted reductant particles will be carried out along with the product Ti powder from the top of the reactor by the exhaust gas, since they have no physical (or called mechanical) trap with Ti powder, they can be easily separated from the Ti powder based on the difference of the physical and chemical properties between the reductant and Ti particles, such as, density, surface zeta potential, magnetic induction, chemical stability, etc.

[0082] A certain gas-flow pattern and turbulence are preferably included in order to ensure that the concentration of HCl in the reactor is controlled by the second reaction, i.e., the reaction between the HCl and the reductant material, which is essential for the success of the process. Further, the continuous existence of excess of reductant in the reactor will increase production rate and product stability.

[0083] The elemental materials and alloys that are produced according to the present invention can by way of example be used in applications in which similar substances produced by other methods may be used and include, but are not limited, to final products, also known as mill products or chunky parts, for the automobile, sports and aerospace industries. The elemental materials and alloys may be incorporated into these applications by, for example, powder metallurgy techniques such as laser sintering, powder injection molding, cold spray and roll forming.

## EXAMPLES

[0084] While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and this application is intended to cover any variations, uses, or adaptations of

the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth and as follows in the scope of the appended claims.

### [0085] Experimental Setup

[0086] The experimental setup for preliminary kinetic investigation consists of an  $H_2$ -Ar gas supply system, a  $TiCl_4$  supplying system, a reactor and a sampling system. A 1"-OD $\times$ 1/8"-thick $\times$ 2'-long inconel tube was used as the outer shell of the reactor chamber. The inconel tube was a nickel-based alloy (~75% wt of Ni, ~15% Cr and ~7% Fe), which can operate at temperature up to 1300° C. In order to prevent the reactions of the inconel tube with  $TiCl_4$  vapor and reductant metals, a 3/4"-OD $\times$ 1/8"-thick $\times$ 2'-long quartz tube was inserted inside the inconel tube as the inner reaction chamber. A Lindberg/Blue tube furnace (Asheville, N.C.) was used to heat the reactor, which enables one to increase the temperature up to 1100° C.

[0087]  $H_2$  and Ar were supplied from the standard commercial cylinders. 1/4"-ID stainless steel tubes were used for the  $H_2$ , Ar and  $TiCl_4$ -vapor flow-in transfer. A 1/2" stainless steel tube was used between the reactor and the sampler for the exhaust gas and particle flow-out transfer.  $TiCl_4$  was provided as liquid from a stainless steel reservoir and carried into the reactor as vapor by  $H_2$ /Ar.

[0088] In order to avoid the oxygen leaking into the reactor, the inside pressure of the reactor was kept slightly (1-3 psig) above ambient under the designed mass flow rate. The various reaction temperatures in the kinetic study were tested. The reaction temperature was first started at 600° C. for the selected reductant metal, then gradually increased or decreased at ~100° C. intervals for each run. 0.2 L/min of 1-12 and 0.1 L/min of  $TiCl_4$  vapor of the flow rates were used as the starting values. If necessary, the liquid  $TiCl_4$  tank could be heated to increase the  $TiCl_4$  flow rate (vapor pressure). Mg and Al were tested.

[0089] The experimental procedures were performed in the order by reductant metal powder/pellet loading, Ar purge,  $H_2$  purge, heating,  $TiCl_4$  and reductant metal introducing, seeding, (reaction), cooling, sampling and sample analysis.

### Example 1

[0090] 1 g of Mg powder, (Alfa Aesar, -325 mesh (<44  $\mu m$  in diameter), 99.8% purity), placed in an alumina crucible of 70 (long) $\times$ 10 (wide) $\times$ 5 (high) mm was used as the reductant metal for the  $TiCl_4$  reduction by  $H_2$ . The experiment was carried out by the procedures described above at the temperature of 600° C. for 30 min then at 700° C. for 20 min.

[0091] After the experiment, the color of the 2-mm surface powders in the crucible changed from original gray to black, and their particle sizes changed to 0.5-2 mm. Most of the powders in the bottom of the crucible still retained their original color and size of the Mg powder, while some particles with metallic shining color and sub-millimeter size existed among them, which could be seen by naked eyes. Many particles in the diameters of sub millimeters with black or metallic shining colors were found in the down-

stream reaction tube and the Sampling Vessel. The samples were separately collected from the crucible and the Sampling Vessel and analyzed by scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX) and X-ray diffraction spectroscopy (XRD).

[0092] SEM-EDX detected that about 5% and about 30% of the materials in the powders collected from the crucible was titanium and magnesium, respectively. Some of the titanium particles were trapped with the magnesium particles and some stood separately. More importantly, the results from SEM-EDX analysis indicates that the powders collected from the Sampling Vessel contained about 70% of titanium but no magnesium at all. The vapor pressure of magnesium at 700° C. is calculated as 0.00987 atm, which is not sufficient to reduce  $TiCl_4$  to titanium powder. Therefore, the powders, particularly collected in the Sampling Vessel should be produced via the  $TiCl_4$  reduction by  $H_2$ . More discussion about this is made in example 2 below. XRD indicated the existence of crystallized Ti in the sample collected from the crucible and found a certain amount of titanium monoxide ( $TiO$ ) in the sample collected from the Sampling Vessel.  $TiO$  is believed to be formed from the oxidation of particulate Ti metal during the sampling process.

### Example 2

[0093] A control experiment was carried out to confirm the function of and the route through the reducing gas, for example,  $H_2$ , for the present invention. The experiment was conducted in the same way as example 1 except that Ar substituted  $H_2$  (no  $H_2$  was used at all). After the experiment, no particle was found in the Sampling Vessel and downstream tubes, which was different from the result of example 1, where a certain amount of the particles were founded from the Sampling Vessel and the downstream tube. Therefore, as discussed above, the particles in the Sampling Vessel and the downstream tube in example 1 were produced via the  $TiCl_4$  reduction through  $H_2$ .

### Example 3

[0094] The experimental condition used was the same as Example 1 except that the reaction was carried out at 900° C. for 30 min then at 1000° C. for 20 min. After the experiment, the color and size of all of the powders in the crucible were changed. In the crucible orientation, the color of all of the powders in the upstream half (about 35 mm long) of the crucible became black, while the color of the powders in the downstream half (~35 mm long) of the crucible became white. Most of the powders in the crucible were in the size range of sub-millimeters to 2 millimeters. SEM-EDX detected the black powders contained about 75% of titanium and about 5% of Mg, and the white powders contained about 70% of Mg and 2% Ti. The black powder was metallic titanium, while the white powder was  $MgCl_2$ . Similar to Example 1, SEM-EDX also indicated that the powders collected from the Sampling Vessel and the downstream tubes contained about 50% of titanium but no magnesium at all.

### Example 4

[0095] 1 g of Al powder, (Alfa Aesar, -325 mesh (7-15  $\mu m$  in diameter), 99.5% purity), placed in the alumina crucible

was used as the reductant metal for the  $TiCl_4$  reduction by  $H_2$ . The experiment was carried out following the procedures described above at 550 and 600° C. for 60 and 30 min, respectively both of which were below the Al melting point of 660° C. After the experiment, about 1-mm-thick surface powders in the crucible were changed from the original gray color to black and from the original 7-15  $\mu m$  particle size to sub-millimeters and millimeters. A small amount of particles were formed in the downstream tubes. SEM-EDX detected the powder and flake samples collected from the top of the crucible contained about 20% and 40% of Ti, and 60% and 34% of Al, respectively. XRD indicated that the powder consisted of a large quantity of  $Ti_0.36Al0.64$  alloy. For the powder sample collected from the downstream tube, the concentrations of Ti and Al were found by SEM-EDX as about 23% and 4%, respectively.

### Example 5

[0096] The experimental condition used was the same as Example 3 except that the reaction was carried out at 700° C. for 30 min then at 750° C. for 20 min, which was above the Al melting point of 660° C. After the experiment, the color and size of all of the powders in the crucible were changed. About 20% of the powders changed from the original gray color to black and from the original 7-15  $\mu m$  particle size to sub-millimeters and millimeters. The rest of unreacted Al powder changed to one big piece with a dimension of about 50 (long)  $\times$  5 (wide)  $\times$  2 (high) mm and a metallic Al color. A small amount of the particles were formed in the downstream tubes. XRD detected that a large quantity of  $Al_xTi_y$  alloy and a certain amount of Ti metal and  $TiO$  existed in the sample collected from the crucible. The ratio of Al to Ti in the alloy varied from  $Al_3Ti$  to  $AlTi$ , which was different from the results discussed in Example 4 above.

### What is claimed:

1. A method of producing an elemental material comprising:
  - (a) combining a precursor material with a reducing gas, to form an elemental material and a first reaction product, wherein said precursor material comprises a halide of an elemental material; and
  - (b) exposing said first reaction product to a reductant material to form a reductant-halide.
2. A method according to claim 1, wherein said reductant-halide has a lower formation free energy than said precursor material.
3. The method of claim 1, wherein said precursor material is in the form of a halide vapor or droplet or mixture thereof.
4. The method of claim 1, wherein the reducing gas comprises at least one substance selected from the group consisting of  $H_2$ ,  $H_2S$ ,  $NH_3$ ,  $CH_4$ ,  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$ ,  $CH_3NH_2$ ,  $CH_3SH$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_2H_5Cl$ ,  $C_3H_4$ ,  $C_3H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_4H_8$ ,  $C_5H_{12}$ ,  $CF_4$ ,  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ ,  $CHF_2Cl$ ,  $CHFCl_2$ ,  $CF_3-CF_3$ ,  $CF_3-CF_2Cl$ ,  $CF_2Cl-CFCl_2$ ,  $D_2$ ,  $B_2H_6$ ,  $GeH_4$ , and  $SiH_4$ .
5. The method of claim 1, wherein the elemental material comprises at least one substance selected from the group consisting of Ti, Al, Sb, Be, B, Ga, Mo, Nb, Ta, Zr, V, Rh, Ir, Os, Ru, Pt, Pd, Re, and U.
6. The method of claim 1, wherein the reductant material is a solid or a liquid or a mixture thereof.

7. The method of claim 6, wherein the reductant material comprises at least one substance selected from the group consisting of Al, Mn, K, Na, Li, Ba, Ca, Mg, Be, Ce, Cs, Hf, Pa, Rb, Sr, Th, U and Zr.

8. The method of claim 2, wherein the precursor material is comprised of one or more of the moieties selected from the group consisting of Cl, Br and F.

9. The method of claim 3, wherein the halide vapor or droplet is one or more of  $TiCl_4$ ,  $VCl_4$ ,  $NbCl_5$ ,  $MoCl_4$ ,  $GaCl_3$ ,  $UF_6$ ,  $ReF_6$ .

10. The method of claim 2 further comprising using an inert gas as a carrier gas for said precursor material.

11. The method of claim 10, wherein the inert gas comprises Ar, He, N<sub>2</sub> or mixtures thereof.

12. The method of claim 2, wherein said combining comprises introducing the halide vapor or droplet submerged in the reducing gas; said reducing gas is static or flowing; said reductant is a solid or liquid metal; and said elemental material is a powder.

13. The method of claim 2, wherein there is an excess of the reductant material over the stoichiometric quantity needed to react with the halide vapor or droplet.

14. The method of claim 13, wherein said excess is greater than six percent.

15. The method of claim 1, further comprising using a seed.

16. A method of producing an alloy comprising:

(a) combining a precursor material with a seed and a reducing gas, to form said alloy and a first reaction product, wherein said precursor material comprises a halide of an elemental material; and

(b) exposing said first reaction product to a reductant material to form a second reaction product.

17. A method according to claim 16, wherein said seed comprises an element that is the same as an element in the precursor material and/or one or more substances that can form an alloy with the element material in the precursor.

18. A method according to claim 17, wherein said seed comprises at least one substance from the group consisting of Al, Be, B, Fe, Ga, Mo, Nb, Sb, Ta, V and Zr.

19. A method of producing an alloy comprising:

(a) combining at least two precursor materials with a reducing gas, to form an alloy and at least one first reaction product, wherein said at least two precursor materials comprise halides of elemental materials; and

(b) exposing said at least one first reaction product to a reductant material to form at least one second reaction product.

20. A method according to claim 19, wherein one of said at least two precursor materials comprises  $TiCl_4$ .

21. A method of producing elemental Ti comprising:

(a) combining a  $TiCl_4$  with a reducing gas selected from the group consisting of H<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, and CH<sub>4</sub> to form Ti and a first reaction product; and

(b) exposing said a first reaction product to a reductant material selected from the group consisting of Al, Mn, Mg, Na, Ca, Li, K, Ba, Be, Ce, Cs, Hf, Pa, Rb, Sr, Th, U, Zr, CrO<sub>2</sub>, CsO<sub>4</sub>, KO<sub>2</sub>, KO<sub>4</sub>, NaO<sub>3</sub>, NaO<sub>4</sub>, RhO<sub>4</sub>, UO<sub>2</sub>, and VO to form a second reaction product.

\* \* \* \* \*



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**United States Patent [19]****O'Donnell et al.****[11] Patent Number:** **5,397,375****[45] Date of Patent:** **Mar. 14, 1995**

**[54] PROCESS FOR THE PRODUCTION OF METALLIC TITANIUM AND INTERMEDIATES USEFUL IN THE PROCESSING OF ILMENITE AND RELATED MINERALS**

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**[57] ABSTRACT**

The invention relates to a process for the production of metallic titanium, characterized in that the process comprises reducing a titanium-fluorine compound selected from titanium tetrafluoride and any hexafluorotitanate soluble in a molten fluoroaluminate, with metallic aluminum in a molten fluoroaluminate. A process for the production of intermediates useful in the processing ilmenite and related minerals is also described.

**7 Claims, No Drawings**

**PROCESS FOR THE PRODUCTION OF METALLIC TITANIUM AND INTERMEDIATES USEFUL IN THE PROCESSING OF ILMENITE AND RELATED MINERALS**

This invention relates to a process for the production of metallic titanium and intermediates useful in the processing of ilmenite and related minerals.

Australia is the major world producer of ilmenite which is exported for about A \$75 per tonne. The cost of metallic titanium in ingot form is about A\$20,000 per tonne. In a more refined form, for example, as the titanium-based alloy from which jet engine fan blades are fabricated, the value of metallic titanium is very much greater. Metallic titanium is, by comparison with most other metals and alloys, very resistant to chemical corrosion and is in great demand in the manufacture of chemical plants and for heat-exchangers and other units in power plants. Another important application is the use of metallic titanium in surgical and dental implants and supports. On a strength-for-weight basis, metallic titanium is stronger than steel and is widely used in the construction of supersonic military aircraft. A cheaper manufacturing route to the production of titanium would make feasible its use in civil aircraft to replace aluminium alloys which have proved to be subject to fatigue failure. This is one of the many applications in which the light, strong and non-corrosive metallic titanium would find wide commercial usage, if available more cheaply than from current processes.

Currently, metallic titanium is produced commercially by two closely related processes. Titanium tetrachloride ( $TiCl_4$ ) is reduced by either metallic sodium (Na) or magnesium (Mg). Each process yields an initial material called "titanium sponge" which may contain 10 to 20% of sodium chloride (NaCl) or magnesium chloride ( $MgCl_2$ ) as products of the initial reaction. To avoid inclusion in the sponge of chlorides of titanium in lower oxidation states (e.g.  $TiCl_2$  or  $TiCl_3$ ), excess reducing metal (Na or Mg) is also in the sponge. Both methods of production are batch processes and the sponge, on solidification after reaction, must be removed from the reactor manually. It is reported that jack-hammers and even explosives are used. The sponge is then purified at least three times by vacuum arc-melting. The processes are both labour and energy intensive.

We have now found that a free-flowing powder of metallic titanium can be produced by employing a process which is similar to conventional aluminium smelting.

According to the present invention there is provided a process for the production of metallic titanium, characterized in that the process comprises reducing a titanium-fluorine compound selected from titanium tetrafluoride and any hexafluorotitanate soluble in a molten fluoroaluminate, with metallic aluminium in a molten fluoroaluminate.

The preferred titanium-fluorine compound is an alkali hexafluorotitanate, more preferably, sodium hexafluorotitanate ( $Na_2TiF_6$ ) or potassium hexafluorotitanate ( $K_2TiF_6$ ).

Preferably the molten fluoroaluminate is a hexafluoroaluminate, more preferably, cryolite ( $Na_3AlF_6$ ).

In one particular embodiment of the invention, sodium hexafluorotitanate ( $Na_2TiF_6$ ) or potassium hexafluorotitanate ( $K_2TiF_6$ ) is dissolved in cryolite ( $Na_3AlF_6$ ) at about 1000° to 1100° C. and metallic alumin-

ium (Al) is added. Aluminium is chosen as the reductant because it is compatible with the melt, being oxidized in the first instance to aluminium fluoride ( $AlF_3$ ) and then interacting with sodium fluoride (NaF) to form cryolite ( $Na_3AlF_6$ ). In addition, aluminium is much less energy-intensive and cheaper to produce than sodium or magnesium reductants used in the current processes.

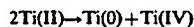
Recovery of metallic titanium is achieved as a consequence of the relative densities of the reactants and the molten medium. Aluminium is less dense than cryolite which, in turn, is less dense than metallic titanium. Therefore, metallic titanium has a tendency to collect at the bottom of the reaction bath and may be tapped from that position with molten cryolite.

The overall reaction for the reduction of  $Na_2TiF_6$  by aluminium to metallic titanium in cryolite occurs in accordance with the equation:



The pure compound  $Na_3AlF_6$  constitutes a neutral molten medium. If the melt is deficient in NaF, i.e. contains an excess of  $AlF_3$ , the medium is acidic. If the melt contains an excess of NaF, then the medium is basic.

$Na_2TiF_6$  may be reduced by aluminium to metallic titanium directly in acidic or basic cryolite i.e. the direct reduction from Ti(IV) to Ti(0) may occur. However, the ultimate reduction to the metal is preferably carried out in neutral cryolite. Under neutral conditions Ti(IV) needs to be reduced only to Ti(II), which will disproportionate spontaneously in neutral medium according to the following equation:



Metallic titanium i.e. Ti(0) is produced, and the Ti(IV) regenerated by the disproportionation reaction is available for reduction by aluminium to Ti(II) and subsequent disproportionation. This cyclic process continues until all Ti(IV) is reduced to Ti(0).

Advantageously  $Na_2TiF_6$  is added progressively to the cryolite bath in order to minimise loss of volatile  $TiF_4$  which might result from thermal decomposition of  $Na_2TiF_6$ . Sodium fluoride (NaF) may be added with  $Na_2TiF_6$  preferably in the ratio 2:1 in order to maintain neutrality of the molten cryolite in accordance with the above equation. Aluminium may be added in a stoichiometric amount or in excess.

It will be appreciated that the process of the present invention may form the basis of a continuous process similar to that used for aluminium smelting. In one approach  $Na_2TiF_6$ , Al and NaF may be added to the cryolite medium, in which case the product of the reaction is cryolite itself. A mixture of molten cryolite and the suspended metal may then be tapped from the bottom of the reactor. The solid material produced may then be crushed and initial separation of cryolite and titanium metal carried out by any suitable known technique, for example, flotation or cyclone separation. Any cryolite remaining attached to the titanium metal particles may be dissolved away from the titanium metal using any solution based on a metal cation which will complex with fluoride ions, preferably a solution of a water soluble aluminium compound, such as a solution of aluminium nitrate.

Since the process of the present invention is similar to conventional aluminium smelting, an alternative proce-

dure of electrowinning may be used in which  $\text{Na}_2\text{TiF}_6$  and  $\text{AlF}_3$  are added continuously to a cryolite bath, Ti being deposited at a graphite cathode. Advantageously a sacrificial anode reaction could be utilized.  $\text{AlF}_3$  would need to be added in the correct stoichiometric amount relative to  $\text{Na}_2\text{TiF}_6$  (4:3) in order to maintain neutrality in the cryolite.

The feedstock for the process of the present invention is preferably  $\text{K}_2\text{TiF}_6$  or  $\text{Na}_2\text{TiF}_6$ . It will be understood however that other sources of titanium may be used, such as,  $\text{TiF}_4$ . A major disadvantage of  $\text{TiF}_4$  is that it reacts readily with atmospheric moisture to form hydrogen fluoride and is difficult and dangerous to handle, whereas  $\text{Na}_2\text{TiF}_6$  and  $\text{K}_2\text{TiF}_6$  are stable in moist air and safe and easy to handle.

We have now developed a process for the safe and easy conversion of  $\text{TiF}_4$  to  $\text{K}_2\text{TiF}_6$  or  $\text{Na}_2\text{TiF}_6$ . In its broadest aspect, this process may be used for the production of intermediates useful in the processing of ilmenite and related minerals.

Further according to the present invention there is provided a process for the production of intermediates useful in the processing of ilmenite and related minerals, characterized in that the process comprises:

- a) dissolving a metal fluoride compound in an organic solvent;
- b) adding an ammonium fluoride to the metal fluoride compound dissolved in the organic solvent in step a) to precipitate an ammonium fluorometallate from the organic solvent; and
- c) dissolving the ammonium fluorometallate from step b) in water and adding an alkali fluoride to produce an alkali fluorometallate and an ammonium fluoride.

The related minerals may include, for example, other titaniferous ores such as rutile, titaniferous slags or zircon.

The organic solvent from step b) may be optionally recycled to step a) and the ammonium fluoride from step c) may be optionally recycled to step b).

Preferably the metal fluoride compound in step a) is selected from titanium tetrafluoride, zirconium tetrafluoride and tin tetrafluoride.

The metal fluoride compound in step a) is often contaminated with an impurity such as a metal oxidefluoride, for example, titanium oxidefluoride. As titanium oxidefluoride is insoluble in organic solvents, this impurity can be separated from the titanium fluoride compound by dissolving the mixture in an organic solvent. The metal oxidefluoride impurity remaining as a residue after treatment with the organic solvent can be heated to produce the desired metal fluoride compound and a metal oxide. The metal oxide may then be treated to produce a metal oxide pigment or a refractory ceramic or recycled to produce metal fluoride compounds such as  $\text{TiF}_4$  or  $\text{ZrF}_4$ .

The organic solvent in step a) is preferably an alcohol, such as, for example, methanol or ethanol.

Preferably the ammonium fluoride in step b) is selected from ammonium fluoride ( $\text{NH}_4\text{F}$ ) or ammonium bifluoride ( $\text{NH}_4\text{HF}_2$ ).

The ammonium fluorometallate produced in step b) may be ammonium fluorotitanate, such as, for example, ammonium hexafluorotitanate ( $(\text{NH}_4)_2\text{TiF}_6$ ) or ammonium fluorozirconate, such as, for example, ammonium heptafluorozirconate ( $(\text{NH}_4)_3\text{ZrF}_7$ ) and ammonium hexafluorozirconate ( $(\text{NH}_4)_2\text{ZrF}_6$ ). Preferably, the ammonium fluorometallate is ammonium hexafluorotita-

nate ( $(\text{NH}_4)_2\text{TiF}_6$ ) which may be used to produce  $\text{K}_2\text{TiF}_6$  or  $\text{Na}_2\text{TiF}_6$  which is the preferred feedstock employed in the process for the production of metallic titanium described above.

5 Preferably the alkali fluoride in step c) is potassium fluoride (KF) or sodium fluoride (NaF).

The alkali fluorometallate produced in step c) may be  $\text{K}_2\text{TiF}_6$  or  $\text{Na}_2\text{TiF}_6$  which is the preferred feedstock employed in the process for the production of metallic titanium described above.

In an alternative process, water and optionally base is added to the metal fluoride compound dissolved in the organic solvent in step a) to produce a hydrated metal oxide.

15 The hydrated metal oxide product from the alternative process may be treated to produce a metal oxide pigment or a refractory ceramic.

In a further alternative process, the ammonium fluorometallate from step b) is pyrohydrolysed to produce a 20 hydrated metal oxide, an ammonium fluoride and hydrogen fluoride.

The ammonium fluoride may be optionally recycled to step b).

The hydrogen fluoride may be optionally treated with silicon dioxide and an alkali fluoride to produce an alkali fluorosilicate. The alkali fluorosilicate may then be heated to produce silicon tetrafluoride and an alkali fluoride. The silicon tetrafluoride may be optionally recycled for use in the process for the formation of 30  $\text{TiF}_4$  from minerals such as ilmenite and the subsequent conversion of  $\text{TiF}_4$  to  $\text{TiO}_2$  as described in our co-pending Australian Patent Application No. 48186/90.

The further alternative process may be performed using any suitable pyrohydrolysis technique. In a particularly preferred embodiment, a flow system having air with entrained water vapour may be streamed over a bed of the ammonium fluorometallate at temperatures sufficiently low to prevent sublimation of, for example,  $\text{TiF}_4$  from a fluorotitanate (200°–300° C.) or  $\text{ZrF}_4$  from 40 a fluorozirconate (450°–500° C.). After an appropriate reaction time, typically 4 to 5 hours, the residues are hydrated  $\text{TiO}_2$  or  $\text{ZrO}_2$ . Volatile HF and  $\text{NH}_4\text{F}$  are carried out of the reaction zone in the air stream and may be condensed to form solid  $\text{NH}_4\text{F}$  and an aqueous solution of HF. The solid  $\text{NH}_4\text{F}$  may be optionally recycled to step b).

The HF may be treated with  $\text{SiO}_2$  and KF or NaF to form  $\text{K}_2\text{SiF}_6$  or  $\text{Na}_2\text{SiF}_6$  which may be recovered and heated to about 600° to 700° C. to yield  $\text{SiF}_4$  which is recycled to a mineral reactor bed to produce further  $\text{TiF}_4$  and  $\text{ZrF}_4$  as disclosed in Australian Patent Application No. 48186/90. The KF or NaF residues may be recycled to step c). 100% recovery of  $\text{TiO}_2$  or  $\text{ZrO}_2$  and all of the fluoride in the compounds volatilized during pyrohydrolysis has been demonstrated experimentally for pyrohydrolysis of  $(\text{NH}_4)_2\text{TiF}_6$  and  $(\text{NH}_4)_3\text{ZrF}_7$  under such conditions.

The  $\text{TiO}_2$  and  $\text{ZrO}_2$  produced by the pyrohydrolysis in the further alternative process are hydrated and therefore more chemically reactive than the  $\text{TiO}_2$  and  $\text{ZrO}_2$  obtained from conventional processes. In the conventional processing of ilmenite and related minerals such as zircon, high-temperature oxidation or hydrolysis reactions are used to convert intermediates into titanium dioxide ( $\text{TiO}_2$ ) or zirconium dioxide ( $\text{ZrO}_2$ ). In the chloride process for pigment-grade  $\text{TiO}_2$  production, titanium tetrachloride ( $\text{TiCl}_4$ ) is burned in oxygen above 1000° C. to produce  $\text{TiO}_2$ . In the conventional production of  $\text{ZrO}_2$ , zircon is fused with alkaline mate-

rials at about 1000° C. and then leached with aqueous solution. Sometimes the zircon is pre-heated by plasma techniques to about 2000° C. before leaching. As a result the TiO<sub>2</sub> and ZrO<sub>2</sub> products obtained in these conventional processes are refractory not particularly amenable to subsequent purification or other processing.

The invention is further described in and illustrated by the following Examples. These Examples are not to be construed as limiting the invention in any way.

#### EXAMPLE 1

A mixture of about 30g Na<sub>3</sub>AlF<sub>6</sub> and 1.9 g of K<sub>2</sub>TiF<sub>6</sub> was melted at 1090° C. in a graphite crucible with a loose-fitting graphite lid. The inert gas argon was bubbled through a graphite lance dipping into the melt. A total of 0.28g of Al and 0.67 g of NaF was added during the reaction by introducing several small compressed pellets of Al and NaF through the lance. After a period of settling, the melt was returned to room temperature and the graphite crucible was sectioned. A black powder was found to have settled towards the bottom of the solidified melt. When this black powder was washed free of cryolite with anhydrous hydrogen fluoride, the powder was shown by electron microprobe analysis to contain metallic titanium. Ignition of the black powder in air produced white titanium dioxide. Aqueous aluminium nitrate solution was shown subsequently to be effective in dissolving the cryolite away from the black powder.

#### EXAMPLE 2

3.60 g of a commercial, crude sample of TiF<sub>4</sub> containing large amounts of titanium oxidefluoride as an impurity, was stirred for several hours in methanol. The resulting solution was separated from the white insoluble residue and added to a saturated solution of NH<sub>4</sub>HF<sub>2</sub> in 250 ml of methanol. An insoluble white precipitate of (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> was formed immediately. After filtration, washing with methanol and drying in air, the mass of (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> was 5.10 g, corresponding with an initial weight of 3.19 g of TiF<sub>4</sub> in the crude starting sample.

This example demonstrates the ease of recovery of (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> from TiF<sub>4</sub> and the efficiency of the separation by dissolution in methanol of TiF<sub>4</sub> from accompanying oxidefluorides.

#### EXAMPLE 3

0.318g of (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> produced as in Example 2 in 5 ml H<sub>2</sub>O was added dropwise to a solution of 0.218 g of

KF in 1 ml of water, cooled in an ice bath. The gelatinous white precipitate formed was collected by filtration and washed with 5 ml of ice-cold water to remove KF. Drying at 105° C. yielded 0.287 g of anhydrous, pure K<sub>2</sub>TiF<sub>6</sub>. The filtrate was reduced by boiling to one-third of its volume and cooled to 0° C. A second yield of 0.088 g of K<sub>2</sub>TiF<sub>6</sub> was collected. Overall, the conversion rate of (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> to K<sub>2</sub>TiF<sub>6</sub> was 97%. Under process conditions, product recovery could be optimised by using a solution saturated with K<sub>2</sub>TiF<sub>6</sub> throughout.

#### EXAMPLE 4

0.1232g of (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> produced as in Example 2 was pyrohydrolyzed at 200°-250° C. for 5 hours. The weight of hydrated TiO<sub>2</sub> after pyrohydrolysis was 0.0524 g, representing a nominal recovery of 105%. When this material was dehydrated by calcining, the weight of TiO<sub>2</sub> was 0.0499 g, representing 100.4% recovery. Analysis for total fluoride in the NH<sub>4</sub>HF<sub>2</sub> sublimate and in the aqueous condensate containing HF indicated 99.3% recovery.

#### EXAMPLE 5

Three pyrohydrolyses at 450°-500° C. for periods of 4 to 5 hours of (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub> produced in a similar manner to Example 2 resulted in indicated recoveries of 99%, 101% and 103% for ZrO<sub>2</sub> and 99%, 102% and 104% for total fluoride.

We claim:

1. A process for the production of metallic titanium comprising reducing a titanium-fluorine compound selected from titanium tetrafluoride and any hexafluorotitanate soluble in a molten fluoroaluminate, with metallic aluminium in a molten fluoroaluminate.
2. A process as claimed in claim 1, wherein the titanium-fluorine compound is an alkali hexafluorotitanate.
3. A process as claimed in claim 2, wherein the alkali hexafluorotitanate is sodium hexafluorotitanate (Na<sub>2</sub>TiLF<sub>6</sub>) or potassium hexafluorotitanate (K<sub>2</sub>TiF<sub>6</sub>).
4. A process as claimed in claim 1, 2, or 3, wherein the molten fluoroaluminate is a hexafluoroaluminate.
5. A process as claimed in claim 4, wherein the hexafluoroaluminate is cryolite (Na<sub>3</sub>AlF<sub>6</sub>).
6. A process as claimed in claim 4, wherein the hexafluoroaluminate is neutral cryolite (Na<sub>3</sub>AlF<sub>6</sub>).
7. A process as claimed in claim 1, 2, or 3, wherein the alkali fluoride is added so as to preserve the stoichiometry and the neutrality of the molten fluoroaluminate.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
CERTIFICATE OF CORRECTION

PATENT NO. : 5,397,375  
DATED : March 14, 1995  
INVENTOR(S) : Thomas A. O'Donnell et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

On the title page, item [54] and column 1, lines 2-5, change the title to  
--PROCESS FOR THE PRODUCTION OF METALLIC TITANIUM--.

Signed and Sealed this  
Fifth Day of September, 1995

Attest:

*Attesting Officer*



BRUCE LEHMAN

*Commissioner of Patents and Trademarks*

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICANT: Jawad Haldar ) Group Art Unit: 7414  
SERIAL NO: 10/560,804 )  
FILED: December 15, 2005 ) Examiner: Zhu, Weiping  
TITLE: A METHOD AND APPARATUS FOR THE PRODUCTION OF METAL ) Docket: CU-4560  
COMPOUNDS

THE COMMISSIONER FOR PATENTS  
P.O. Box 1450  
Alexandria, VA 22313-1450

**AFFIDAVIT UNDER 37 CFR 1.132**

I, Jawad Haldar, the inventor named in the application for letters patent of the United States for an invention entitled A METHOD AND APPARATUS FOR THE PRODUCTION OF METAL COMPOUNDS, Serial No. 10/560,804, filed December 15, 2005, declare as follows:

1) I am a scientist working for the Commonwealth Scientific and Industrial Research Organisation (CSIRO). CSIRO is the Australian Government's main national research laboratory and is classified by the International Scientific Institute (ISI) among the top research institutions in the world. Before joining CSIRO in 1990, I obtained a Doctorate degree and a Master degree from the University of Paris (France). My research career includes extensive work on electric arcs, electric discharges, modelling of arc welding, plasma vapour deposition and materials synthesis. My work on arc discharges led to the discovery of important basic phenomena in arc physics and in the late 1990s I developed the first ever numerical simulation of droplet formation of arc welding. My experimental activities also included developing technologies for nanopowder production and physical vapor deposition of tetrahedral carbon. I regularly attend scientific conferences and receive and read numerous scientific journals. I am the sole inventor of the invention the subject of the present application.

2) I have been asked to review the patent specification for US patent no. 5,032,176 (Kametani et al) and describe its relevance (if any) to the invention the subject of the present application. The method disclosed by Kametani et al. does not use aluminium as a reducing agent. In col 12, lines 5-10, it is stated that the purpose of including aluminium with the reducing agent is to produce a titanium-aluminium composite powder, suggesting that the aluminium is not the reducing agent as it is

conserved through the reduction process. Indeed, it is well known to me that reactions between titanium chlorides and magnesium (or sodium) are more favourable than reactions between titanium chlorides and aluminium. The Gibbs free energy for reacting  $TiCl_4$  with Al is -102 kJ/mole while this energy is -468 kJ for Mg and -800 kJ/mole for Na. This means that in the presence of Mg or Na,  $TiCl_4$  is unlikely to react with anything else.

3) Figures 1 and 2 below depict the results of calculations I have recently performed for the reactions which are theoretically possible for chemical compositions having a mixture of  $TiCl_4 + 2Mg + 2Al$  in Figure 1 and  $TiCl_4 + 4Na + 2Al$  in Figure 2. For Mg, Na and Al, the stoichiometric amount required to reduce 1 mole of  $TiCl_4$  are respectively 2 moles, 4 moles and 1.33 moles. Including excess Al in the calculations in Figures 1 and 2 is intended to show that the presence of excess Al does not improve reactivity between  $TiCl_4$  and Al. The results in Figures 1 and 2 were obtained using Outokumpu HSC chemistry, a renowned commercial package, and clearly show zero reactions between  $TiCl_4$  and Al. This confirms to me that, in the presence of Mg or Na,  $TiCl_4$  will not react with Al. The amount of  $AlCl_3$  formed in both cases is nil. Thus, it is my understanding that because Kometani et al require the presence of either Na or Mg, if Al were added for alloying with Ti to form a Ti-Al alloy, the Al would not react at all with  $TiCl_4$ .

4) To emphasise this point, in Figure 3 I show the results of a similar calculation for a composition including 10 moles of Al. Here, even with the presence of highly excessive amounts of Al relative to Na, there are absolutely no reactions between  $TiCl_4$  and Al. The results in Figures 1,2 and 3 prove to me that for the method disclosed by Kometani wherein titanium tetrachloride is reduced by molten agent including Mg or Na, Al cannot be a reducing agent when present in the molten reducing agent.

5) I have also been asked to consider and describe what reactions would be likely to occur if Al were to act as a reducing agent in the methods described in Kometani. Kometani requires his reactions to occur at 650 C (The temperature required for  $TiCl_4$  throughout the specifications). Reactions between Al and  $TiCl_4$  at 650 C, is a one step process leading directly to formation of  $Al_3Ti(solid)$  and  $AlTi(solid)$  (as is depicted in Figure 3 of the article by Murphy which was also cited by the Examiner). As such, at a temperature of 650 C (~900 K), the reaction between  $TiCl_4$  and Aluminium would be a single step reduction process and not a two-step process as is the case in the present application. Our technology attempts to solve

problems associated with the one step process, namely the formation of multi-phase compounds (Al<sub>3</sub>Ti and AlTi as in Murphy-Figure 3).

6) I have also been asked to review a paper by Dr A. B. Murphy entitled 'Equilibrium calculations of the reduction of titanium tetrachloride by aluminium and hydrogen', published in *High Temperature Chemical Processes*, volume 3, pp. 365-374 (1994), and describe its relevance (if any) to the methods described in Kametani et al and to the invention the subject of the present application.

7) The results of Murphy are relevant only in extreme conditions at high temperatures in excess of 3000 K wherein all reactants are gaseous, as clearly explained in Section 4 of his paper. For the invention the subject of the present application, reactions typically start at less than 200 °C (~450 K) and then the temperature is increased to 1000 °C (1273 K). Also, for the present application in Stage 1 of the process, Al powder or flakes with a limited surface area are used, and Stage 2 of the process is purely based on solid-solid reactions. Thus, whilst the results of Murphy indicate that reactions between TiCl<sub>4</sub> and Al can occur, they are not directly relevant to the invention the subject of the present application.

8) I would not relate the results of Murphy as depicted in the paper mentioned above and the disclosure of Kametani for several reasons: a)- in the presence of Mg or Na as in Kametani, TiCl<sub>4</sub> would not react with Al, b)- the results of Murphy are not valid at the temperatures required by Kametani, and c)- Murphy clearly states that his results may be useful for applications in production of titanium-aluminium alloys only if the reactants are heated to high temperatures and then cooled to condense the resulting gases; this goes opposite to the teaching of Kametani.

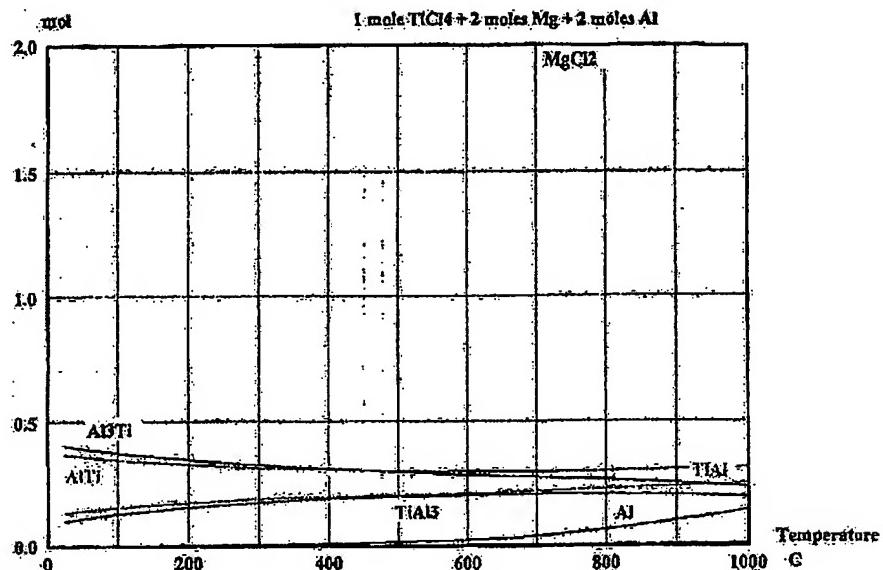


Figure 1: Equilibrium composition for a mixture of 1 mole  $\text{TiCl}_4$  + 2 moles  $\text{Mg}$  + 2 moles  $\text{Al}$ .

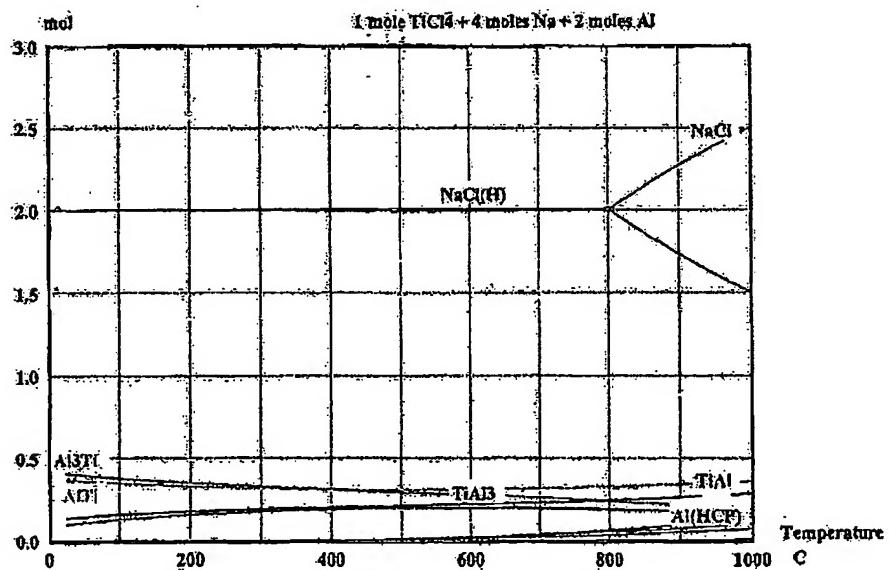


Figure 2: Equilibrium composition for a mixture of 1 mole  $\text{TiCl}_4$  + 4 moles  $\text{Na}$  + 2 moles  $\text{Al}$ .

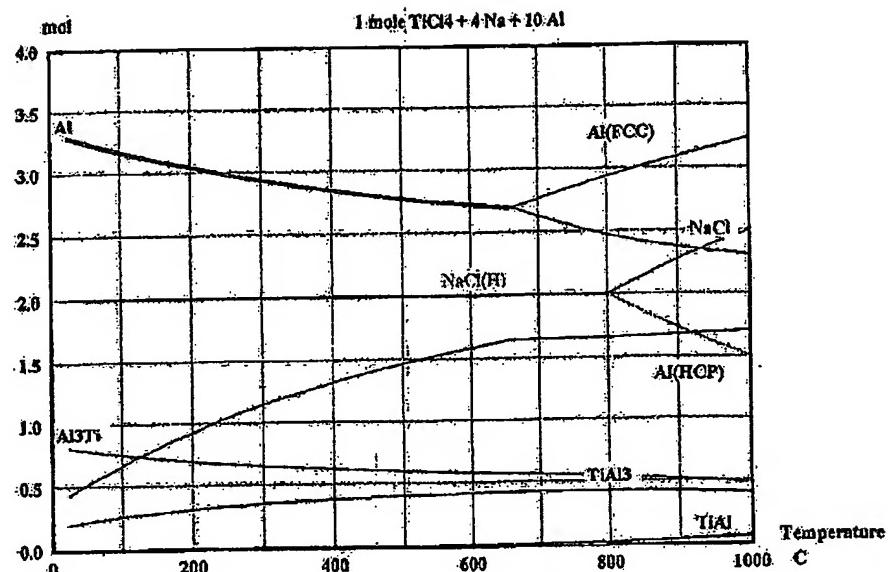


Figure 3: Equilibrium composition for a mixture of 1 mole  $\text{TiCl}_4$  + 4 moles  $\text{Na}$  + 10 moles  $\text{Al}$ .

I further declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: May 1<sup>st</sup>, 2009

  
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Jawad Haider

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICANT: Jawad Haidar ) Group Art Unit: 7414  
SERIAL NO: 10/560,804 )  
FILED: December 15, 2005 ) Examiner: Zhu, Weiping  
TITLE: A METHOD AND APPARATUS FOR THE PRODUCTION OF METAL  
COMPOUNDS ) Docket: CU-4560

THE COMMISSIONER FOR PATENTS  
P.O. Box 1450  
Alexandria, VA 22313-1450

**AFFIDAVIT UNDER 37 CFR 1.132**

I, Anthony B Murphy, the first author of the paper 'Equilibrium calculations of the reduction of titanium tetrachloride by aluminium and hydrogen', published in *High Temperature Chemical Processes*, volume 3, pp. 365-374 (1994), declare as follows:

- 1) This paper presents the results of theoretical calculations of the composition of mixtures of argon, hydrogen, aluminium and titanium tetrachloride, performed under the assumption of chemical equilibrium. The calculations indicate that, for some mixtures of the above substances, solid titanium and solid titanium aluminides can be formed at temperatures below about 3000 K.
- 2) In interpreting the results of these calculations, it is vital to take into account the assumption of chemical equilibrium that underlies the calculations. Chemical equilibrium calculations are based on the assumption that all chemical reactions run to completion. For this assumption to be valid, the following must all be true:
  1. The reactants for each reaction must have sufficient energy to overcome the energy barrier for that reaction;
  2. There must be sufficient time allowed for each reaction to run to completion;
  3. The reactants must be able to make good contact with each other, so that the reactants should all be in the gas or possibly liquid phase. Alternatively, one reactant could be in solid form, but should have a very large surface area to volume ratio (e.g., be in nanopowder form) to allow good contact with the other reactants.
- 3) Each of these three requirements is favoured by high temperatures. At high temperatures, requirement 1 is more likely to be satisfied because the reactants have greater energy, requirement 2 is more likely to be satisfied because reaction

rates are higher, and requirement 3 is more likely to be satisfied because the reactants are more likely to be in the gas phase.

4) The paper was written to assess the viability of conversion of titanium tetrachloride to titanium using aluminium or hydrogen or both aluminium and hydrogen combined as reducing agents. As is made clear in Section 4 of the paper, the scheme that was being assessed involved heating of all reactants to a temperature at which only gaseous species were present, about 3000 K or higher. The gas mixture would then be cooled sufficiently slowly to allow chemical reactions to run to completion. As the mixture cooled, liquid and solid substances would be formed. The calculations presented in the paper predicted that some conditions these substances would be titanium and titanium aluminides.

5) The methods used in the paper are not suited to the calculation of reactions involving solid reactants, because the reactants do not make good contact with each other, and diffusion of chemical species through solids is very slow. Further, at the lower temperatures at which condensed species are present, the reactants are less likely to have sufficient energy to overcome energy barriers, and the rates of reactions are slower. Hence the chemical equilibrium assumption is not appropriate, and the calculations are not applicable.

I further declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: May 1, 2009

  
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Anthony B Murphy